

AD-A068 889

EUREKA CO BLOOMINGTON IL EUREKA ADVANCE SCIENCE DIV
ADVANCED THERMAL BATTERIES.(U)
DEC 78 D M RYAN

F/G 10/3

UNCLASSIFIED

AFAPL-TR-78-114

F33615-77-C-3147

NL

1 OF 2

AD 68889



AFAPL-TR-78-114

LEVEL

2
NW

AD A068889

ADVANCED THERMAL BATTERIES

THE EUREKA COMPANY
EUREKA ADVANCE SCIENCE DIVISION
1201 E. BELL STREET
BLOOMINGTON, ILLINOIS 61701

DDC
RECEIVED
MAY 24 1979
C

DDC FILE COPY

DECEMBER 1978

INTERIM REPORT FOR PERIOD SEPTEMBER 1977
THRU SEPTEMBER 1978

Approved for public release; distribution unlimited

AIR FORCE AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

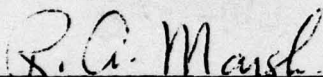
79 05 23 037

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



R. A. MARSH, Project Engineer
Batteries & Fuel Cells



ROBERT R. BARTHELEMY
Chief, Energy Conversion Branch

FOR THE COMMANDER



JAMES D. REAMS
Chief, Aerospace Power Division

If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFAPL/POE-1, W-PAFB, OH 45433 to help us maintain a current mailing list.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. PERFORMER'S CATALOG NUMBER	
18 AFAPL TR-78-114			
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED	
6 Advanced Thermal Batteries		9 Interim Rept Sep 77 - Sep 78	
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)	
10 David M. Ryan		15 F33615-77-C-3147 new	
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
The Eureka Company Eureka Advance Science Division 1201 E. Bell Street Bloomington, Illinois 61701		16 31452285 17 22	
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE	
Air Force Aero Propulsion Laboratory/POE-1 Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, Ohio 45433		11 December 1978	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES	
12 105p.		105	
		15. SECURITY CLASS. (of this report)	
		Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)			
Approved for public release; distribution unlimited			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
Work done under Air Force Contract Nr. F33615-77-C-3147 with The Eureka Company			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
Thermal Battery, Lithium-Aluminum Anode, Sodium Tetrachloroaluminate Anolyte, Molybdenum Pentachloride catholyte, Low Temperature Activation, Acid-Base Study, Cupric Chloride Catholyte			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
<p>The feasibility of building thermal batteries with cells composed of an anode of LiAl alloy, a cathode of a heavy metal chloride and a NaAlCl₄ electrolyte has been demonstrated. Engineering research is now being done to further characterize and improve this battery system.</p> <p>A commercial source of NaAlCl₄ has been tested and found to be quite satisfactory for the preparation of battery materials. Various lithium</p>			

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

79 05 23 037

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

alloys (viz., 20 w/o LiAl, 40 w/o LiAl, and LiSi) have been characterized and found to be alternate anode materials. The relative amount and nature of the binder or antilow agent present in the electrolyte powders has been investigated. Various cathode powders including FeS₂, FeCl₃, CuCl₂, WCl₆ and MoCl₅ have been characterized and evaluated. It has been found that MoCl₅ is superior for making high energy density batteries and CuCl₂ is superior for long life applications. FeS₂ has been found to function only at temperatures too high for consideration with this system. The acid-base nature of the electrolyte has been exploited and the acidic materials make superior cells.

The electrolyte, cell and battery fabrication processes have been so improved that the batteries can now be made quite reliably with repeatable and predictable performances.

The energy density of the basic cell has been improved 300%. The battery has been demonstrated to function well across the entire required test temperature spectrum. It has been found that the skin temperature is higher than expected but the current carrying capacity is better than expected. The fully engineered battery is already being considered for application in an ordnance missile system.

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	SPECIAL
A	

PREFACE

This report describes development of technology for an advanced thermal battery to be used for ordnance applications. This effort began with electrochemical technology resulting from research by the Air Force Frank J. Seiler Research Laboratories. The next effort was a battery engineering feasibility study completed by the Eureka Advance Science Corporation under Contract F33615-76-C-2080. This effort demonstrated that a thermal battery with a LiAl alloy anode, a NaAlCl_4 anolyte, and a catholyte made primarily with MoCl_5 was at least feasible. However, the work under the above contract was extremely limited in scope due to both time and funding limitations and, as a result several very promising applications and techniques were not investigated. This new effort, Contract F33615-77-C-3147, provides for further exploratory development and optimization of an advanced thermal battery system.

The submitted date for this report was February, 1979, covering effort completed during the interval 15 September 1978 thru 15 September 1979.

The cognizant Air Force project officer was Mr. R. A. Marsh, AFAPL/POE-1, Wright-Patterson Air Force Base, Ohio. The technical support rendered by Mr. W. S. Bishop of the project officer's organization was very beneficial and greatly appreciated. The consultation and technical support of Lt Col Lowell King, Major John Erbacher, Capt Chuck Hussey, Lt John Nardi and Capt Larry Vaughn of the Air Force Frank J. Seiler Research Laboratory, Air Force Academy, Colorado was outstanding and a major contribution to the program.

TABLE OF CONTENTS

SECTION	DESCRIPTION	PAGE
I	INTRODUCTION	1
II	A COMMERCIAL SOURCE OF NaAlCl_4	3
III	NaAlCl_4 ANALYSIS	6
IV	PARTICLE SIZE GROWTH IN CATHOLYTES	11
V	CAB-O-SIL FOR ANOLYTE PREPARATION	15
VI	LiCl AS AN ELECTROLYTE ADDITIVE	17
VII	ALTERNATE BINDERS	20
VIII	ACID-BASE PROPERTIES OF THE ELECTROLYTE	22
IX	ALTERNATE CATHODE CHLORIDES	42
X	ALTERNATE CATHODE MATERIALS (<u>NOT</u> CHLORIDES)	64
XI	BINDER ADDED TO CATHOLYTE	67
XII	BINDERS (NOT CAB-O-SIL) IN THE CATHOLYTE	68
XIII	FREON BLENDING	68
XIV	ALTERNATE ANODE ALLOYS	69
XV	CELL REPRODUCIBILITY	78
XVI	CELL COMPATABILITY	79
XVII	CELL PROCESSING AND FABRICATION	80
XVIII	BATTERY BUILDING AND TESTING	80
XIX	CONCLUSION	91

LIST OF ILLUSTRATIONS

FIGURE	DESCRIPTION	PAGE
1a & 1b	DSC FINGERPRINT SPECTRA	8
2	DIFFERENTIAL SCANNING CALORIMETRY USED TO MONITOR MOISTURE IN ANOLYTES	9
3a	YELLOWISH WHITE CRYSTALS IN $\frac{1}{2}$ " SQUARE SECTION SAMPLE TUBE	13
3b	YELLOWISH WHITE CRYSTALS COLLECTED FOR ANALYSIS	13
4	SINGLE CELL TEST RESULTS FOR CELLS MADE WITH VARIOUS AMOUNTS OF CAB-O-SIL IN THE ANOLYTE	16
5	SINGLE CELL TEST DATA FOR CELLS MADE WITH VARIOUS AMOUNTS OF CAB-O-SIL IN THE ANOLYTE	16
6	SINGLE CELL DISCHARGE CURVES ILLUSTRATE THE "SPIKE" FORMED BY ADDING LiCl TO THE ANOLYTE	19
7	SINGLE CELL TESTS RESULTS	30
8	SINGLE CELL TEST RESULTS WHICH COMPARE FeCl_3 WITH MoCl_5	45
9	TYPICAL DISCHARGE CURVES FOR FeCl_3 & MoCl_5	46
10	PEAK VOLTAGE VS. CURRENT DENSITY COMPARISONS FOR MoCl_5 , CuCl_2 , AND FeCl_3	47
11	A COMPARISON OF TEMPERATURE TOLERANCE FOR FeCl_3 , CuCl_2 , AND MoCl_5	47
12	SINGLE CELL DISCHARGE PROFILES FOR A $\text{MoCl}_5/\text{FeCl}_3$ TYPE CELL	51
13	A TYPICAL CuCl_2 SINGLE CELL DISCHARGE CURVE COMPARED TO A TYPICAL MoCl_5 DISCHARGE CURVE	53
14	CuCl_2 IS SUPERIOR TO MoCl_5 AT THE LOW CURRENT DENSITIES	54
15	TYPICAL DISCHARGE CURVES FOR FeCl_3 , CuCl_2 AND $\text{FeCl}_3/\text{CuCl}_2$ TYPE CELLS	57

LIST OF ILLUSTRATIONS - CONTINUED

FIGURE	DESCRIPTION	PAGE
16	WC1 ₆ SINGLE CELL TEST RESULTS COMPARED TO MoCl ₅ TEST RESULTS	59
17	TEMPERATURE TOLORANCE OF WC1 ₆ COMPARED TO MoCl ₅	60
18	A TYPICAL WC1 ₆ DISCHARGE CURVE	60
19	A TYPICAL CuCl ₂ /WC1 ₆ DISCHARGE CURVE	61
20	POLARIZATION CURVES FOR THE NaAlCl ₄ SYSTEM COMPARED TO THE KCl-LiCl SYSTEM	62
21	A COMPARISION OF LiAl AND LiSi SINGLE CELL TEST RESULTS	73
22	THE TEMPERATURE TOLERANCE OF LiSi CELLS	74
23	THE EFFECT OF LiSi UPON A TYPICAL MoCl ₅ DISCHARGE CURVE	75
24	A SCHEMATIC DIAGRAM OF A WRIGHT-PATTERSON TEST BATTERY	82
25	THE USEFUL ENERGY DENSITY OF THE CELL HAS NEARLY TRIPLED IN ONE YEAR	93

LIST OF TABLES

TABLE	DESCRIPTION	PAGE
1	SINGLE CELL TEST RESULTS FOR KAOLIN CONTAINING POWDERS	21
2	SINGLE CELL TEST RESULTS FOR KAOLIN CONTAINING CELLS - SPECIFIC RESISTIVITIES	21
3	TYPICAL ACID-BASE SINGLE CELL TESTS FOR CuCl_2 CELLS USING A 40 w/o LiAl ANODE	25
4	TYPICAL ACID-BASE SINGLE CELL TESTS FOR MoCl_5 CELLS USING A 40 w/o LiAl ANODE	27
5	THE EFFECT OF VARIOUS TEST LOADS ON CuCl_2 CELLS MADE WITH THE FOUR DIFFERENT POSSIBLE COMBINATIONS OF ACIDIC ANOLYTE, ACIDIC CATHOLYTE, BASIC ANOLYTE AND BASIC CATHOLYTE	29
6	THE EFFECT OF VARIOUS TEST TEMPERATURES ON CuCl_2 CELLS MADE WITH FOUR DIFFERENT POSSIBLE COMBINATIONS OF ACIDIC ANOLYTE, BASIC ANOLYTE, ACIDIC CATHOLYTE, BASIC CATHOLYTE	31
7	AVERAGE VOLTAGE, STANDARD DEVIATION AND 1 σ BANDS FOR THE FOUR DATA SETS IN TABLE 5	32
8	INTERNAL RESISTANCE FOR TYPICAL CELLS OF EACH OF THE FOUR TYPES TESTED	33
9	INTERNAL RESISTANCE FOR CuCl_2 CELLS OF EACH OF THE FOUR TYPES TESTED WITH CONSTANT TEMPERATURE AND A VARIABLE LOAD	34
10	INTERNAL RESISTANCE FOR CuCl_2 CELLS OF EACH OF THE FOUR TYPES TESTED WITH CONSTANT LOAD RESISTANCE AND A VARIABLE TEST TEMPERATURE	35
11	INTERNAL RESISTANCES OF MoCl_5 CELLS OF EACH OF THE FOUR DIFFERENT TYPES	36
12	THE EFFECT OF VARIOUS CURRENT DENSITIES ON MoCl_5 CELLS AT CONSTANT TEMPERATURE AND WITH THE FOUR POSSIBLE ACID-BASE TYPES	37
13	THE EFFECT OF VARIOUS TEST TEMPERATURES AT CONSTANT LOAD FOR MoCl_5 CELL WITH A 40 w/o LiAl ANODE AND A BASIC ANOLYTE AND ACIDIC CATHOLYTE	37

LIST OF TABLES - CONTINUED

TABLE	DESCRIPTION	PAGE
14	TYPICAL SINGLE CELL TEST RESULTS FOR CuCl_2 CELLS MADE WITH THE FOUR POSSIBLE COMBINATIONS OF ACIDIC ELECTROLYTE MIXED WITH KAOLIN	39
15	TYPICAL SINGLE CELL TEST RESULTS FOR CELLS MADE WITH CuCl_2 , AND ACIDIC CATHOLYTE, A BASIC CATHOLYTE, AND USING KAOLIN FOR A BINDER. THE TEST TEMPERATURE WAS 200°C	39
16	INTERNAL RESISTANCE RESULTS FOR CELLS MADE WITH CuCl_2 CATHODES, 40 w/o ANODES, AND ELECTROLYTES WITH MECHANICALLY MIXED KAOLIN FOR A BINDER	40
17	FeCl_3 & 20 w/o LiAl	45
18	SINGLE CELL RESULTS WITH $\text{MoCl}_5/\text{FeCl}_3$ CATHOLYTE AND EITHER, 20 w/o OR ANODE #7	49
19	SPECIFIC RESISTIVITIES OF VARIOUS CELLS COMPARED	51
20	TABULATION OF CuCl_2 SINGLE CELL RESULTS	52
21	CuCl_2 SINGLE CELL TEST RESULTS	55
22	$\text{FeCl}_3/\text{CuCl}_2$ SINGLE CELL TEST DATA	56
23	SINGLE CELL TEST DATA FOR WC1_6 CATHOLYTE	58
24	SINGLE CELL TEST DATA FOR WC1_6 CATHOLYTE	58
25	TABULATION OF FeS_2 SINGLE CELL TEST RESULTS	66
26	SINGLE CELL TEST RESULTS FOR CELLS USING ANODE #3	71
27	SINGLE CELL TEST DATA	72
28	SINGLE CELL TEST DATA	74
29	40 w/o LiAl SINGLE CELL TEST RESULTS	77
30	40 w/o LiAl SINGLE CELL TEST RESULTS	77

LIST OF TABLES - CONTINUED

TABLE	DESCRIPTION	PAGE
31	STORAGE BATTERY TEST RESULTS	83
32	HOT AND COLD BATTERY TEST RESULTS	86
33	HOT AND COLD TESTS FOR BATTERIES MADE WITH 20 w/o LiAl ANODES	86
34	STORAGE AND REPEATABILITY BATTERY TEST RESULTS. THESE BATTERIES WERE TESTED AT ROOM TEMPERATURE ACROSS AN 8 OHM LOAD	87
35	TEST RESULTS FOR BATTERIES MADE WITH 40 w/o LiAl ANODES	87
36	TEST RESULTS FOR BATTERIES MADE WITH 58 w/o LiSi ALLOY	88
37	TEST RESULTS FOR BATTERIES MADE WITH ACIDIC CuCl_2 ELECTROLYTES. THE TEST WAS 50 OHMS	89
38	TEST RESULTS FOR BATTERIES CONSTRUCTED WITH QUINARGO HEAT BUFFERS IN THE CELL CONNECTORS	89
39	BATTERY TEST RESULTS WITH A 25 OHM LOAD	90

SECTION I

INTRODUCTION

It has previously been demonstrated that an advanced thermal battery based on the $\text{LiAl}/\text{NaAlCl}_4/\text{MoCl}_5$ electrochemical system was feasible (Contract #F33615-76-C-2080). The work done under the above feasibility contract was extremely limited in scope due to both time and funding limitations and as a result, several promising materials applications and design/fabrication techniques were not investigated. This most recent effort (Contract #F33615-77-C-3147) provides for further characterizations, development, and optimization of an advanced thermal battery system along with testing of sufficient cells and batteries to establish reliable performance predictions over the range of interest.

This work has a general and specific objective. The general objective is to develop technology for an advanced, long life, compact, lightweight thermal battery for missile and air delivered ordnance applications. This effort will be built upon electrochemical technology resulting from research by the Air Force Frank J. Seiler Research Laboratories and engineering research and development done by the Eureka Advance Science Division to demonstrate the feasibility of using such a system for thermal battery application. The most critical problems such as activation voltage spike; availability of sufficient high purity electrolyte; pellet building and fabrication; etc., should be eliminated or at least controlled. Alternate materials should be investigated to optimize the cell/battery performance. These investigations shall include use of alternate alloys or surface preparation techniques to insure rapid and predictable activation; alternate electrolyte formulations; studies of other cathode reactants such as CuCl_2 , FeS_2 , or other applicable materials; use of

more efficient thermal insulation materials; and use of lightweight structural case materials.

The specific objective of the program is to design and develop a battery which will meet the requirements outlined below. The voltage of the battery should be 28 volts nominal. The battery should be capable of carrying a 2 amp current across a resistive load for 45 minutes. The activation time is less than one second. The electrical noise maximum is 1/2 volt peak to peak. This should not ideally exceed 1 pound or 6 in³. The battery must function at both -65°F and at 165°F. The skin temperature should not exceed 200°F. The battery must also be capable of withstanding other normal thermal battery environments such as storage requirements; vibration, shock, spin, etc.; and other usual thermal battery requirements.

SECTION II

A COMMERCIAL SOURCE OF NaAlCl_4

NaAlCl_4 is a difficult material to prepare. The salts are hygroscopic and volatile. Their vapors are corrosive and poisonous. The Alcoa Aluminum Company has developed a new method of producing AlCl_3 and has become a source of pure NaAlCl_4 . It was the purpose of this experiment to evaluate this material for thermal battery use.

The first sample from Alcoa was received in August, 1977. The second sample was received in September, 1977. The earlier sample was somewhat yellow in color but the second sample was quite white. The material was received in the form of 50 to 100 gram chunks mixed with smaller chips.

When the first sample was received it was tested by a differential scanning calorimeter (DSC). The DSC showed a large endotherm peaking at 167°C . The melting point was at 159°C . The sample was further heated to nearly 290°C and then allowed to cool. The sample froze at 97°C . The sample was reheated and the melting point was at 157°C .

A sample of this material was then mixed with 10 w/o Cab-O-Sil, sealed in a glass container, and heated one hour in an oven at 220°C . When cooled, ground and sieved, this mixture was called Anolyte #102. Another anolyte was made identically like this and it was labeled Anolyte #104. The DSC spectrum of Anolyte #104 yielded a melting point of 152°C . The sample was cooled and reheated. The new melting point was 151°C .

Anolyte #102 was mixed with graphite and MoCl_5 to make a catholyte. The catholyte formula was:

25.43 w/o Anolyte #102

56.50 w/o MoCl_5

18.08 w/o Graphite

This was labeled Catholyte #103. The DSC spectrum of Catholyte #103 provided a melting point of 151°C . This sample was allowed to cool and was then reheated. The new melting point was 147°C .

A second catholyte (Catholyte #101) was made identically like Catholyte #103 except that Anolyte #104 was used instead of Anolyte #102. The melting point of Catholyte #101 was 149°C as measured with the DSC.

A single cell test was performed with cells made from Anolyte #104 and Catholyte #103. The anode was 20 w/o LiAl alloy. The cell formula was:

Anode: 0.277 gm 20 w/o LiAl alloy

Anolyte: 0.935 gm Anolyte #104

Catholyte: 1.039 gm Catholyte #103

The platen temperature was 200°C and the test load was 25 ohms.

Single Cell #101

Peak Voltage (V_p) = 2.34v

Peak Current (I_p) = 93.6 ma

Current Density (i_p) = 18.5 ma/cm^2

Life to 80% Peak (T_{80}) = 960 sec.

Energy Density (E/m) = 21.0 Wh/kg

This cell has the longest 80% lifetime of any single cell test yet reported (for earlier single cell test results see AFAPL-TR-77-12)¹. This long life can be primarily attributed to the absence of a high voltage spike.

A single cell test was also performed upon a cell made with Anolyte #102 and Catholyte #101. In every other respect this single cell test was identical to Single Cell #101.

1. Reference. D. M. Ryan, and L. C. Bricker, "High Energy Density Pelletized Aluminum Chlorine Thermal Batteries," AFAPL-TR-77-12, April, 1977

Single Cell #102

$$V_p = 2.33v$$

$$I_p = 93.2 \text{ ma}$$

$$t_{80} = 960 \text{ sec.}$$

$$E/m = 20.86 \text{ Wh/kg}$$

$$i_p = 18.4 \text{ ma/cm}^2$$

This single cell showed no spike at all.

It is felt that these tests indicate clearly that the Alcoa NaAlCl_4 can make excellent electrolyte for use in this system and can indeed be considered a commercial source of NaAlCl_4 .

A second sample of NaAlCl_4 was received from Alcoa in September, 1977. This sample was whiter than the somewhat yellowish first sample. Some of this material was used to make a test anolyte. A test anolyte is composed of 10 w/o Cab-O-Sil and 90 w/o NaAlCl_4 . This was labeled Anolyte #1002. The DSC spectrum showed a peak at 436°K (163°C) and another broad exotherm at 628°K (355°C). A second sample was tested and both the endotherm (163°C) and the exotherm (347°C, 2nd sample) were reproduced. The melting points measured by the DSC were 151°C and 150°C respectively.

Anolyte #1002 was used to make a test catholyte, Catholyte #1001. A test catholyte is composed of:

Test Catholyte 25.4 w/o test anolyte

56.5 w/o MoCl_5

18.1 w/o graphite

The DSC spectrum of Catholyte #1001 showed an endotherm at 379°K (106°C) and an endotherm at 432°K (159°C) and a confusion of peaks and valleys which start about 470°K (197°C). A second sample was run and the two endotherms were well

reproduced (2nd sample, 105°C & 159°C). Heating of the second sample was stopped at about 200°C and the material was allowed to cool. When the cooled sample was reheated only one endotherm was noticed (159°C). The endotherm at 105°C did not reappear upon the second heating of the sample. It is interesting to note that the area of the second 159°C endotherm was approximately equal to the sum of the areas of the original two endotherms at 105°C and 159°C. If the endotherm at 159°C corresponds to the fusion of NaAlCl_4 , then the melting point of this material was about 152°C and was lowered to 148°C upon reheating. The catholyte appears to react with the aluminum sample pan at about 195°C and this corresponds to the peaks and valleys noted at the hot end of the spectrum. This area is not very reproducible.

SECTION III

NaAlCl_4 ANALYSIS

The physical/chemical properties of NaAlCl_4 depend upon the ratio of sodium and aluminum in the material. Three of the most important properties controlled by composition are conductivity, melting point, and acidity. In addition to these three properties a thermal battery chemist is also interested in moisture contamination. These properties can be monitored by performing two analyses on the NaAlCl_4 :

- 1) Differential Scanning Calorimetry (DSC)
- 2) An acid/base analysis

After many DSC spectra were generated for test electrolytes typical spectra were gradually characterized. A typical DSC spectrum for an anolyte displays two prominent features:

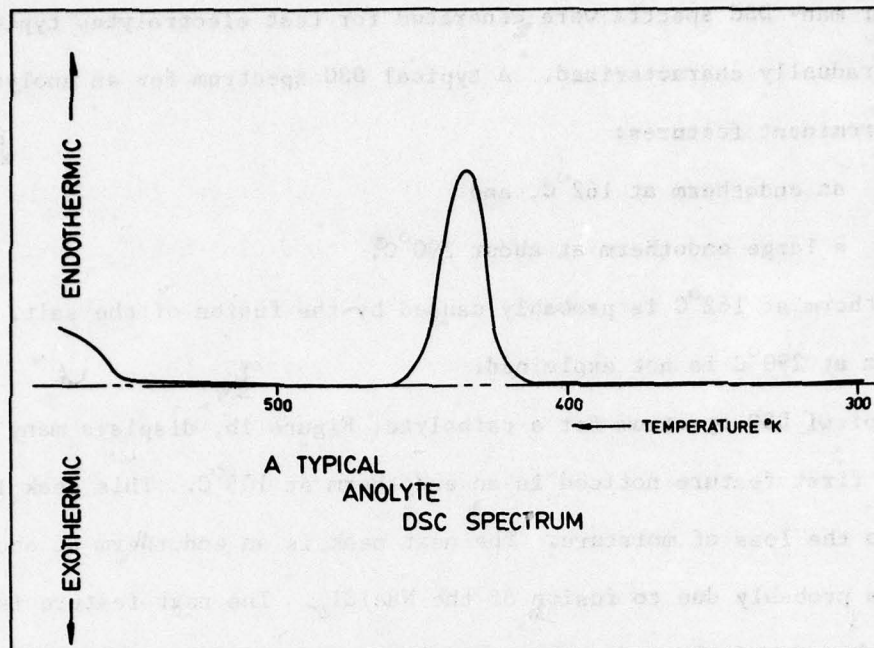
- 1) an endotherm at 162°C , and
- 2) a large endotherm at about 290°C .

The sharp endotherm at 162°C is probably caused by the fusion of the salt. The large endotherm at 290°C is not explained.

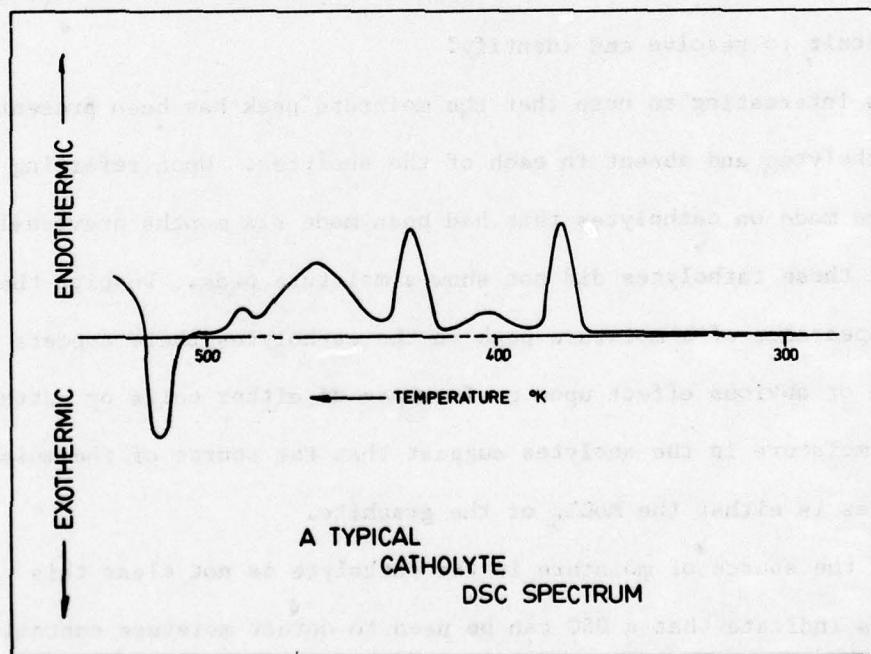
A typical DSC spectrum for a catholyte, Figure 1b, displays many more features. The first feature noticed is an endotherm at 105°C . This peak is probably due to the loss of moisture. The next peak is an endotherm at about 156°C . This is probably due to fusion of the NaAlCl_4 . The next feature is two endotherms, so broad and close together that they sometimes are hard to resolve. These appear at about 189°C and 214°C respectively. The next feature is a strong exotherm at about 258°C . These last two endotherms and exotherm are reproducible, but often difficult to resolve and identify.

It is interesting to note that the moisture peak has been present in each of the catholytes and absent in each of the anolytes. Upon referring to some DSC spectra made on catholytes that had been made six months previously, it is noticed that these catholytes did not show a moisture peak. Despite the contemporary appearance of a moisture peak in the catholytes there appears to be no immediate or obvious effect upon performance of either cells or batteries. The absence of moisture in the anolytes suggest that the source of the moisture in the catholytes is either the MoCl_5 or the graphite.

While the source of moisture in the catholyte is not clear this observation does indicate that a DSC can be used to detect moisture contamination. Accordingly, a DSC spectrum was generated for an anolyte sample. The anolyte was



a. A Typical Anolyte DSC Spectrum



b. A Typical Catholyte DSC Spectrum

Figure 1. DSC Fingerprint Spectra

then exposed to room air and resampled. This was repeated every ten minutes for the first hour. The last sample was taken after overnight exposure to moist air (chemistry laboratory ambient air).

The dry sample had a clear peak at 164°C (See Figure 2). Upon repeated exposure to the moist room air this peak was found to diminish and a new peak began to appear at the temperature range from 131°C to 142°C , increasing in amplitude as the 164°C peak diminished. As the exposure was repeated, the initial 164°C peak and the 137°C peak moved closer together and broadened until it was nearly impossible to resolve the two peaks. Also, after prolonged exposure another peak appeared at about 97°C and then the only two features that remained were the peaks at 97°C and a broad peak at about 151°C .

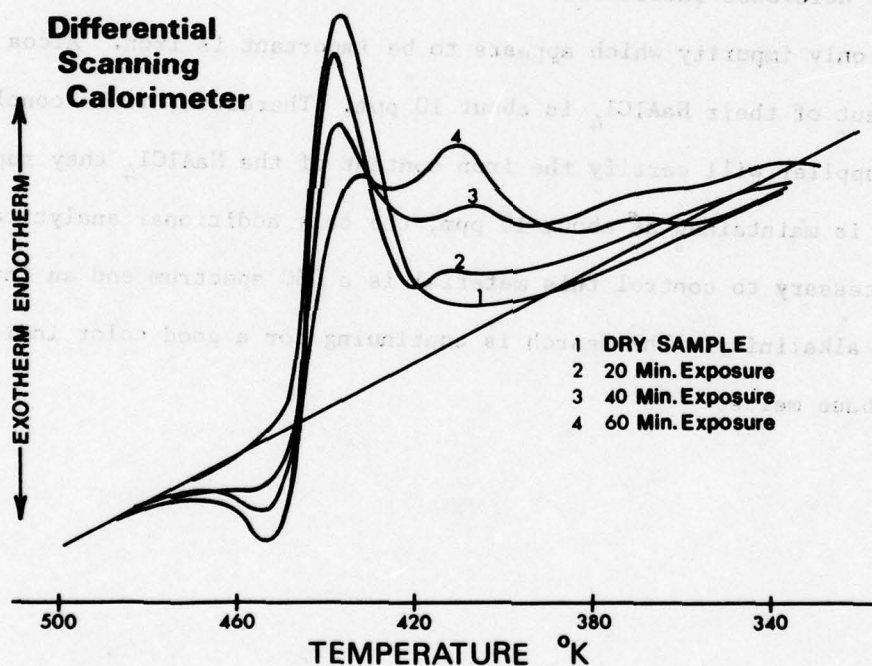


Figure 2. Differential Scanning Calorimetry used to Monitor Moisture in Analytes

Another interesting, but not always repeatable, feature of these spectra was the appearance of an exotherm which sometimes followed the broad endotherm at about 160°C. Figure 2 is an illustration of the above described spectra.

It appears that the absence of hydrolysis products can be monitored by measurement of the relative heights of the peaks at the 160°C range and the 136°C range. For "total" hydrolysis of the sample (ie, exposed overnight), the sample became more endothermic by a factor of 2.8 over the total range 47°C to 327°C.

The most inexpensive, easiest way to monitor the acidity or alkalinity of the NaAlCl_4 would be by addition of a colored "indicator" to the melt. The initial search has so far been unsuccessful. The materials tried have been CoCl_2 , FeCl_3 , S, and NaSCN . Stilbene was tried and did not work as well as some other common organic acid-base indicators.

The only impurity which appears to be important is iron. Alcoa claims the iron content of their NaAlCl_4 is about 10 ppm. Therefore, it is concluded that if the supplier will certify the iron content of the NaAlCl_4 they supply and the level is maintained at about 10 ppm, the only additional analytical procedures necessary to control this material is a DSC spectrum and an indication of acidity or alkalinity. The search is continuing for a good color indicator for acid and base melts.

SECTION IV

PARTICLE SIZE GROWTH IN CATHOLYTES

The thermal cells made for this program are made by filling a cylindrical cavity with electrolyte powders, passing a straight edge across the top of the cavity to make an even upper surface, and compressing the powders to make a round pellet. However, some difficulty has been incurred while making cells with catholytes made with NaAlCl_4 and MoCl_5 . The upper layer cannot be struck off to form a smooth surface because of the presence of some unusually large particles which cause deep furrows to form as the straight edge moves across the top of the cell making cavity. It has been noticed that these large particles are not initially present in the catholyte but appear after storage. It appears that the catholyte particles are growing larger. It was believed that, since the electrolyte materials were so hygroscopic, some product of hydrolysis was probably slowing forming. Therefore, an experiment was performed to investigate the effects of storing MoCl_5 catholytes in atmospheres which contain various amounts of moisture.

Four catholyte samples were stored in four respectively different atmospheres and were periodically examined with a microscope. The catholyte was a regular test MoCl_5 catholyte. Two gram samples of catholyte were placed in a three inch length of 1/2" square section glass tubing. The first sample was stored in ambient chemical laboratory air which had a nominal relative humidity of greater than 50%. The second sample was stored in dry room air which maintained a nominal relative humidity of about 2 1/2%. The third sample was placed in the sample tube while in an argon box and was sealed shut so it contained an atmosphere of dry argon. The fourth sample was similar to #3 except that 20% of the argon was pumped out of the sample tube, refilled with O_2 and then sealed. The atmosphere above sample #4 was 20% O_2 and 80% argon.

The samples were inspected and photographed periodically. The intervals of inspection were:

<u>Inspection</u>	<u>Elapsed Storage Time</u>
1st	None
2nd	1 Hour
3rd	2 Hours
4th	3 Hours
5th	4 Hours
6th	19 Hours
7th	24 Hours
8th	45 Hours
9th	70 Hours
10th	118 Hours
11th	163 Hours

The sample that reacted quickest to the presence of moisture was the sample exposed to moist air. The first evidence of reaction occurred after three hours exposure. After about 24 hours a profuse growth of yellowish-white needle crystals had grown, either on the catholyte surface or, above the surface on the walls of the glass sample tube. The sample exposed to dry room air reacted similarly except that the first changes were not noticed until after about 19 hours of exposure. There were even some small white crystals starting to form in the two sealed samples but these were just barely visible after even 163 hours of elapsed time.

In addition to the profuse growth of large needle crystals there were also some small salmon pink crystals noticed. These appeared in all four samples and are not necessarily hydration products. The identity of these pink crystals is still unknown.

An attempt was made to collect the yellow white crystals for analysis. This was done (Figure 3a & b) but the analysis was unsuccessful. The yellowish-white crystals are still unidentified.

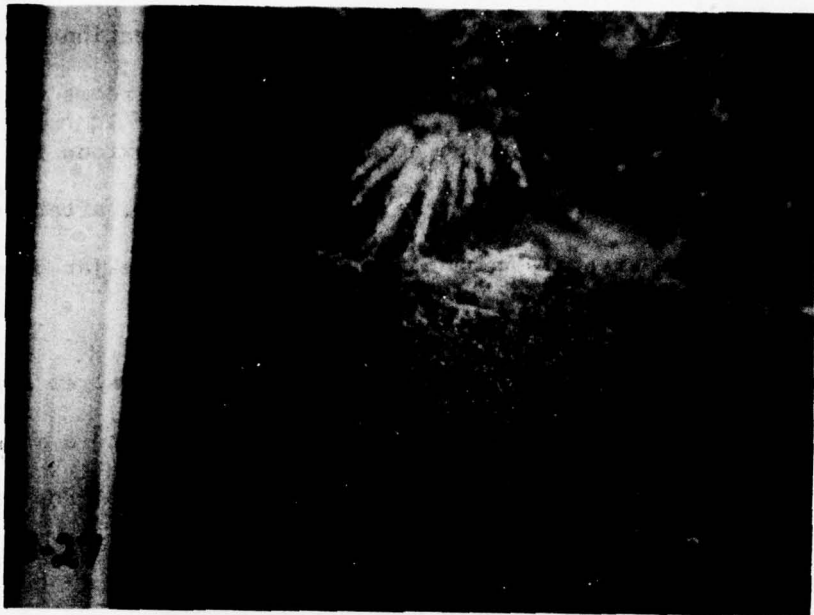


Figure 3a, Yellowish White Crystals in $\frac{1}{2}$ "
Square Section Sample Tube

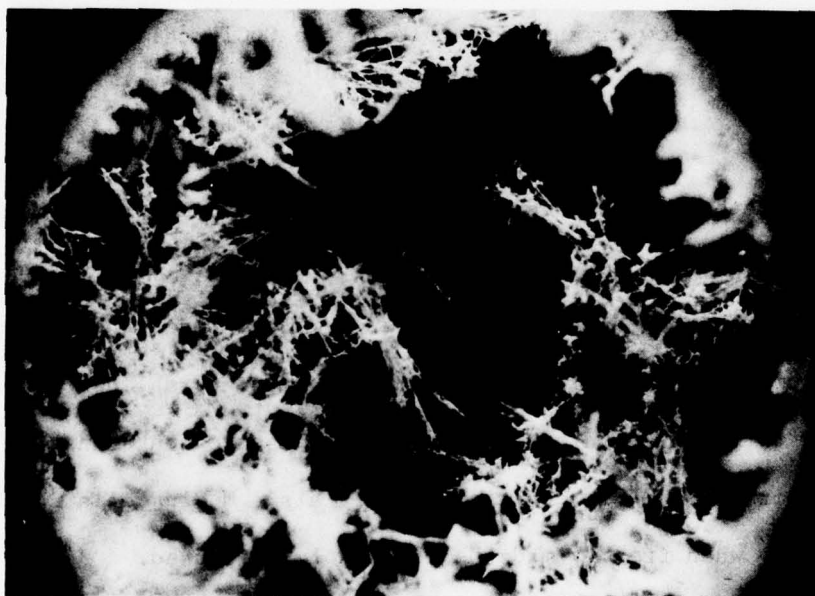


Figure 3b, Yellowish-white Crystals
Collected for Analysis

In addition to this experiment some practical observations can be made. One day an attempt was made to make cells even though the dry rooms were wet (above 3.5% R.H.). The project had to be stopped because a noxious red vapor formed above the catholyte as the cells were being made. Also, after only about 30 minutes small yellowish crystals were noticed forming in the jar of catholyte. The catholyte was obviously reacting to the moisture.

On another occasion a small glass jar with a plastic screw type lid was used to store MoCl_5 cells. This was stored in a dry room next to a jar of CuCl_2 cells. After a couple of weeks the MoCl_5 cells had grown a fine crop of yellow needle crystals on the catholyte layer. After a month the cells bowed badly and cracked. After two months the cells were completely crumbled. During this same time period there was only a slight bowing of the CuCl_2 cells stored in the adjacent jar. After about three months the CuCl_2 cells also cracked and eventually broke. There were never any yellow crystals visible on the CuCl_2 cells.

SUMMARY

A MoCl_5 catholyte has been found to be quite sensitive to moisture. When exposed to moisture large yellow-white needle crystals form on the surface of the catholyte. These crystals are a nuisance which hinder the cell making process. In future cell making projects, more than the normal degree of care is going to have to be given in order to prevent moisture contamination during fabrication or storage of MoCl_5 containing materials. MoCl_5 cells can be made satisfactorily only when freshly made MoCl_5 catholyte is used.

SECTION V

CAB-O-SIL FOR ANOLYTE PREPARATION

Cab-O-Sil is a synthetically prepared siliceous material manufactured and marketed by the Cabot Corporation, Boston, Massachusetts. The thermal battery industry uses this material as a thickening agent to prevent electrolyte flow in activated batteries. As this program began the only percentage of Cab-O-Sil ever tried was 10 ^W/o. An experiment was performed to test the effects of using some other percentage and optimizing the percentage of Cab-O-Sil used to immobilize electrolyte powders.

A series of anolytes containing from 7.4 to 15 ^W/o Cab-O-Sil was prepared. These anolytes were used to prepare corresponding catholytes. These materials were tested with a DSC, made into cells and given single cell tests.

The DSC spectra of these anolytes and catholytes show no changes due to the difference in the amount of Cab-O-Sil present in the anolyte.

The single cell test data have been organized into four groups of 7.4 ^W/o Cab-O-Sil, 10 ^W/o Cab-O-Sil, 13 ^W/o Cab-O-Sil and 15 ^W/o Cab-O-Sil. Curves for 80% life versus current density have been generated for these four groups. The curve for the 15% group is lower than for the curves for the other three groups. The curves for the 7.5 ^W/o, 10 ^W/o, and 13 ^W/o have been collected under one envelope. The data points for the 7.4 ^W/o group are scattered worse than the others. The scatter in the 7.4% group is unexplained except that electrolyte flow was noted for some of these cells. There was a large activation high voltage peak which appeared in the 15% group but was not as pronounced for the other three groups.

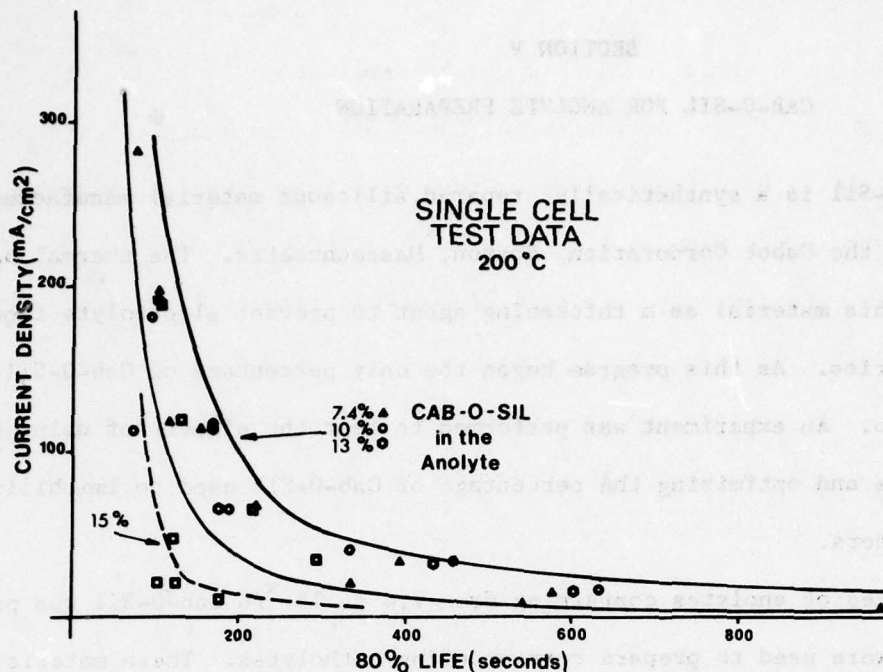


Figure 4. Single Cell Test Results for Cells made with Various Amounts of Cab-O-Sil in the Anolyte

Another set of four curves was generated as test temperature versus energy density (Figure 5). The best data were at 10^{w/o} and the worst were at 15^{w/o}.

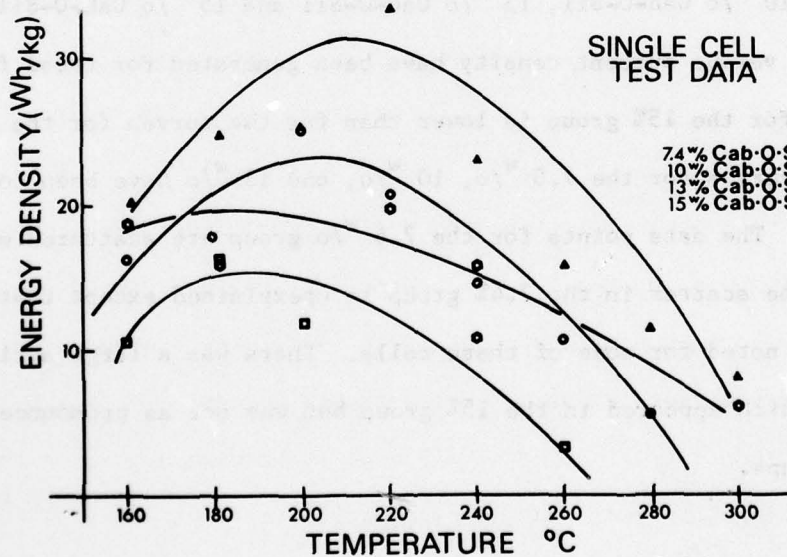


Figure 5. Single Cell Test Data for Cells made with Various Amounts of Cab-O-Sil in the Anolyte

It is the conclusion of this experiment that:

- 1) The contained percentage of Cab-O-Sil in an anolyte has very little effect on cell performance with the range of 10 ^{w/o} to 13 ^{w/o} Cab-O-Sil;
- 2) at the low extreme of 7.4 ^{w/o} Cab-O-Sil there is evidence of electrolyte flow;
- 3) a high percentage of Cab-O-Sil (15 ^{w/o}) increased the activation high voltage peak;
- 4) the optimum percentage of Cab-O-Sil in an anolyte is from 10 ^{w/o} to 13 ^{w/o}.

SECTION VI

LiCl AS AN ELECTROLYTE ADDITIVE

The normal peak voltage expected from a thermal cell with a LiAl anode and a MoCl₅ catholyte is about 2.4 volts (dependent upon how the cell is loaded for testing). However, in some instances in the first few seconds after initiation the peak voltage may be as high as 3.7 volts (again depending on how the cell is loaded). Because this initial high voltage peak appears as a long, narrow, sharp pointed curve on the strip chart made during single cell testing, this phenomenon

has been called "spike" formation. It was believed that perhaps a reaction between lithium and chlorine could produce this high voltage. Therefore it was felt that perhaps the spike formation could be retarded by slowing the lithium reaction. Since Li^+ ions are probably a product of this reaction it was anticipated that adding LiCl to the anolyte would prevent spike formation. It was also felt that adding LiCl would lower the melting point of the electrolyte and, therefore, speed activation.

To test these theories a series of anolytes were prepared which contained different respective amounts of LiCl.

<u>Anolyte Number</u>	<u>% LiCl Contained</u>
A #1016	1 ^{w/o}
A #1018	5 ^{w/o}
A #1022	10 ^{w/o}
A #1024	20 ^{w/o}
A #1026	40 ^{w/o}

The DSC spectra of these LiCl anolytes were similar to all of the other anolyte spectras. It was noticed that the spectra for Anolytes #1022, #1024, and #1026 (10, 20, and 40 ^{w/o}) displayed characteristic moisture peaks while Anolytes #1016, and #1018 (1 and 5 ^{w/o}) did not. It is interesting to note that there was only very little cold voltage noted for cells made with Anolytes #1016 (1 ^{w/o}) or #1022 (10 ^{w/o}) even though #1022 (10 ^{w/o}) had prominent moisture peaks. On the other hand all of the cells made with Anolytes #1018, #1024, and #1026 (5, 20 and 40 ^{w/o}) did display cold voltage even though there were no moisture peaks in the DSC spectrum of Anolyte #1018 (5 ^{w/o}). The peak at 105°C, which is prominent in the catholyte spectra, has been interpreted as a moisture peak, and this peak was present for all of the LiCl containing catholytes.

Single cell tests were made to test these LiCl containing powders. The purpose of the experiment was to reduce the spike formation but the single cell test results showed just the opposite. The results of these tests are illustrated by Figure 6. Adding LiCl to the anolyte greatly increases the spike, and no batteries were ever made with cells containing LiCl.

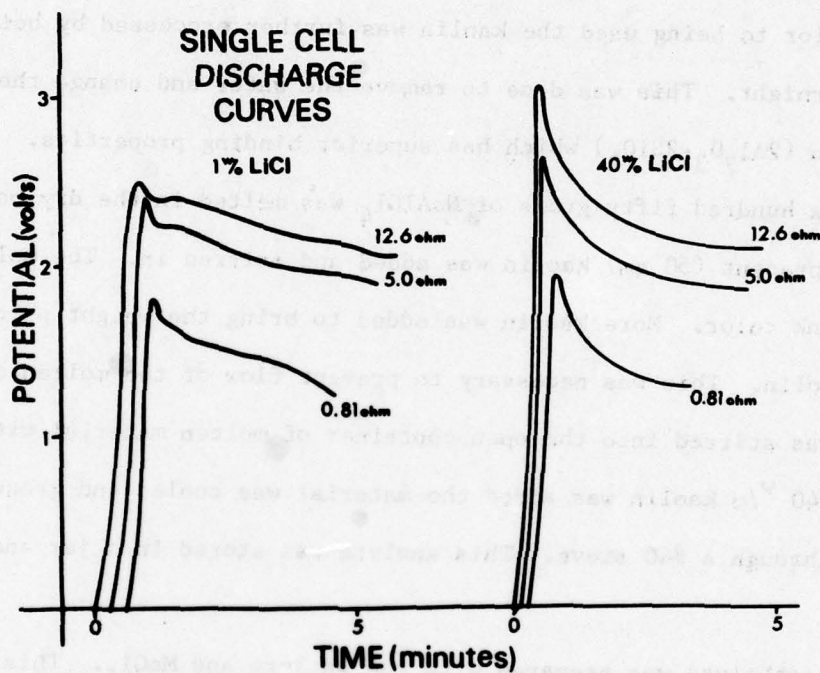


Figure 6. Single Cell Discharge Curves Illustrate the "Spike" formed by Adding LiCl to the Anolyte

SECTION VII

ALTERNATE BINDERS

Florida kaolin ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O}$) is a naturally occurring mineral which is mined, cleaned and purified. This material has been used as a binder (ie., an antiflow agent) in thermal cells for many years and has just recently been replaced by Cab-O-Sil, a synthetic silica. All of the cells made so far for this project have been made with Cab-O-Sil and now cells have been made with kaolin for comparison of electrical properties performance.

Prior to being used the kaolin was further processed by being baked at 485°C overnight. This was done to remove the water and change the structure to metakaolin ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which has superior binding properties.

One hundred fifty grams of NaAlCl_4 was melted in the dry box. Twenty-five weight percent (50 gm) kaolin was added and stirred in. The molten material took on a pink color. More kaolin was added to bring the weight percentage up to 40 % kaolin. This was necessary to prevent flow of the molten electrolyte. The kaolin was stirred into the open container of molten material with a glass rod. After 40 % kaolin was added the material was cooled and ground until it could pass through a #40 sieve. This anolyte was stored in a jar and labeled A #1034.

A catholyte was prepared with the anolyte and MoCl_5 . This was a test catholyte which contained about 10 % kaolin. This was labeled C #1065.

Test cells were made from these materials. Some cells (#1289 thru #1292) were made with 40 % LiAl anode. Cell #1293 was made with 28 % LiAl . Cells #1287 & #1288 were made with Cab-O-Sil catholyte and 40 % LiAl and were control cells for this test. The results of the tests are shown in Tables 1 and 2.

**TABLE 1 SINGLE CELL TEST RESULTS
FOR KAOLIN CONTAINING POWDERS.**

S/N	V _P	i _P	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	LOAD	NOTES	
	volts	mA/cm ³	seconds	seconds	Wh/kg	Wh/kg	ohms		
1288	1.81	204	145	220	32.2	43.7	.81	Cab-O-Sil Catholyte With 40 ^W /o LiAl anode	
1287	2.35	43	642	876	37.7	47.5	5		
1292	2.31	42.3	218	638	12.3	29.4	5	170°C	40 ^W /o Kaolin
1290	2.23	40.8	675	970	35.4	46.6	5	180°C	40 ^W /o LiAl
1289	2.26	41.4	498	732	26.0	35.1	5	200°C	10 ^W /o Kaolin in
1291	2.29	41.9	459	637	25.5	32.6	5	220°C	the Catholyte
1293	2.31	42.3	391	686	21.5	33.5	5	200°C	28 ^W /o LiAl

**TABLE 2 SINGLE CELL TEST RESULTS FOR KAOLIN
CONTAINING CELLS - SPECIFIC RESISTIVITIES.**

S/N	V _P	i _P	t ₈₀	load	Temp	Spec. r at t ₀	Spec. R at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	mA/cm ²	sec.	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1288	1.81	204	145	.81	200	1.31	.955	1.84	-	Cab-O-Sil 40 ^W /o LiAl
1287	2.35	43	642	5	200	.477	.261	.146	1.02	
1292	2.31	42.3	218	5	170	8.20	6.40	5.94	-	Kaolin 40 ^W /o LiAl
1290	2.23	40.8	675	5	180	3.94	-	4.67	2.48	
1289	2.26	41.4	498	5	200	.249	3.11	1.23	6.96	Kaolin & 28 ^W /o LiAl
1291	2.29	41.9	459	5	200	2.67	1.07	1.81	2.47	
1293	2.31	42.3	391	5	200	3.84	7.29	3.58	3.76	

In summary, the cells which contained kaolin did not perform quite as well as the cells that were made with Cab-O-Sil. The voltage was slightly lower and the energy density was slightly lower. The main cause of the lower energy density was the significant increase in the internal cell resistance. The antiflow properties of the kaolin anolyte appeared to be at least as good as the Cab-O-Sil material. Kaolin is easier to handle and easier to incorporate into an anolyte. There is no readily apparent reason to further pursue the substitution of kaolin for Cab-O-Sil.

SECTION VIII

ACID-BASE PROPERTIES OF THE ELECTROLYTE

The effects upon cell and battery performance due to changes in the acid-base properties² of the $\text{NaCl} \cdot \text{AlCl}_3$ mixtures which compose the electrolytes are not well known. It was anticipated that the cathode chloride would be much more soluble in an acidic catholyte than in a basic catholyte. The increased solubility should increase the activity, which would increase the cell voltage. However, the mobility of the cathode active species would also be increased and it was anticipated that as the cathode active materials crossed the electrolyte

2. Reference. A. A. Fannin, Jr., L. A. King, and D. W. Seegmiller, "Chloroaluminate Equilibria in $\text{AlCl}_3 \cdot \text{NaCl}$ Melts," Journal of the Electrochemical Society, 119,801 (1972).

an energy wasting corrosion reaction would take place at the anode as well as the energy producing cell reaction. It was believed that this energy wasting reaction could be retarded by using a suitable separator. If a basic anolyte was used with an acidic catholyte the reduced solubility of the cathode active species in the base would allow the anolyte/catholyte interface to act like a separator. The soluble cathode chloride would not cross the basic anolyte layer.

Another problem anticipated was the higher vapor pressure of acidic NaCl-AlCl_3 mixtures. This could cause problems in safely preparing these electrolyte materials and could cause performance problems for both cells and batteries.

In addition to this it has already been observed that the conductivity of NaAlCl_4 cells decreased dramatically with an increase in acidity of the electrolyte.^{3,4} This is accounted for by an increase in the size of the Al (III) containing species in the acidic electrolytes, a decrease in the concentration of very mobile Na^+ ions, and the formation of a nonconducting Al_2Cl_6 layer at the anode/anolyte interface early in the cell discharge. Once again, some of these effects may be lessened by the use of an acidic catholyte and a basic anolyte.

A number of anolytes and catholytes were prepared for this experiment. These will now be tabulated:

- A #1036 - 10 w/o Cab-O-Sil, NaCl saturated NaAlCl_4 .
- A #1038 - 10 w/o Cab-O-Sil, NaCl saturated NaAlCl_4 .
- A #1040 - A mixture of all of A #1036 & A #1038.
- A #1042 - 10 w/o Cab-O-Sil, 69 m/o AlCl_3 in the NaAlCl_4 ;
heated at 250°C overnight - an "acidic" anolyte.

3. Reference. G. D. Brabson, J. K. Erbacher, L. A. King, and D. W. Seegmiller, "Exploratory Aluminum-Chlorine Thermally Activated Battery: Single Cell Experiments," FJSRL-TR-76-0002, January, 1976.

4. Reference. C. L. Hussey, J. K. Erbacher, L. A. King, "High Energy Density Pelletized Aluminum Chloride Thermal Batteries," FJSRL-TR-76-0003, January, 1976.

- A #1044 - 40 ^{w/o} kaolin, 69 ^{m/o} AlCl₃ in the NaAlCl₄;
mixture mechanically mixed and not heated -
an acidic anolyte.
- A #1046 - 40 ^{w/o} kaolin, NaCl Saturated NaAlCl₄; mixture
mechanically mixed and not heated - a basic anolyte.
- C #1067 - A test catholyte with 56 ^{w/o} MoCl₅, 26 ^{w/o} A #1036,
and 18 ^{w/o} graphite.
- C #1069 - A test catholyte with 56 ^{w/o} MoCl₅, 26 ^{w/o} A #1040,
and 18 ^{w/o} graphite.
- C #1071 - A mixture of three old CuCl₂ catholytes approximately
1 part C #1059, 2 parts C #1051, and 2 parts C #1057.
- C #1073 - A test catholyte made of 56 ^{w/o} CuCl₂, 26 ^{w/o} A #1042,
and 18 ^{w/o} graphite - This is an "acidic" catholyte.
- C #1075 - A test catholyte made of 56 ^{w/o} MoCl₅, 26 ^{w/o}
A #1040, and 18 ^{w/o} graphite - A basic MoCl₅ catholyte.
- C #1077 - A test catholyte made of 56 ^{w/o} MoCl₅, 26 ^{w/o} A #1042,
and 18 ^{w/o} graphite - An "acidic" MoCl₅ catholyte.
- C #1079 - A catholyte - 56.4 ^{w/o} CuCl₂, 30.6 ^{w/o} A #1044, and
13 ^{w/o} graphite - An "acidic" kaolin catholyte.
- C #1081 - A catholyte made of 56 ^{w/o} CuCl₂, 26 ^{w/o} #1042, and
18 ^{w/o} graphite - This is an "acidic" catholyte.
- C #1083 - A test catholyte approximately 3 parts C #1081 and
1 part C #1073.

The first single cell tests done for the acid-base experiments were
with cells using CuCl₂ catholytes and 40 ^{w/o} LiAl anodes. There were four types
of cells made:

- 1) basic anolyte and basic catholyte - these were control cells for the rest of the experiment.
- 2) basic anolyte and acidic catholyte
- 3) acid anolyte and acidic catholyte
- 4) acidic anolyte and basic catholyte

Representative tests of each type of cell were done with a 5 ohm load and at a temperature of 200°C. The following table represents these results.

TABLE 3 TYPICAL ACID-BASE SINGLE CELL TESTS
FOR CuCl_2 CELLS USING A 40 % LiAl ANODE

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	TEMP. & LOAD	NOTES:
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg		
1294	1.87 +	34.2 +	551 +	773 +	20.9 +	26.2 +	200° & 5 ohms	Basic Anolyte Basic Catholyte
1295	1.87 +	34.2 +	593 +	824 +	22.3 +	28.4 +		Acidic Anolyte Basic Catholyte
1306	1.86 +	34.0 +	963 +	1536 +	35.0 +	50.1 +		Acidic Anolyte Acidic Catholyte
1310	1.90 +	34.8 +	781 +	1440 +	29.4 +	47.5 +		Basic Anolyte Acidic Catholyte

These cell tests are not individual cells but, rather, the average of three similar cells. Single Cell #1294 was just a normal test cell and was the control cell for this experiment. These results can be compared to cell tests 1270 & 1271 which were reported two months previous to this experiment and which were constructed similarly to cell #1294. The results of the earlier cell tests can be summarized like this:

$$V_p = 1.78V$$

$$i_p = 34.2 \text{ mA/cm}^2$$

$$t_{80} = 600 \text{ seconds}$$

EARLIER CELLS

$$t_{70} = 1200 \text{ seconds}$$

$$ED_{80} = 24 \text{ Wh/kg}$$

$$ED_{70} = 40 \text{ Wh/kg}$$

The later cell tests, which were done for this experiment, were made with different, but similar, batches of anolyte and catholyte and can be summarized like this:

$$V_p = 1.78V$$

$$i_p = 34.2 \text{ mA/cm}^2$$

$$t_{80} = 550 \text{ seconds}$$

LATER CELLS

$$t_{70} = 750 \text{ seconds}$$

$$ED_{80} = 21 \text{ Wh/kg}$$

$$ED_{70} = 26 \text{ Wh/kg}$$

These two sets of single cell data provide some information on the normal variation in cell performance. Considering this large variation there is little difference in the performance of cell #1294 and cell #1295. As predicted cell #1310 had the highest voltage but this could have been due to statistical variance as well as to the effects of using an acidic catholyte with a basic anolyte. Single cell #1306 had significantly longer life and a greater energy density than any of the other cells. Yet, this cell was made with both, an acidic anolyte and an acidic catholyte, and it was predicted that this combination would have the shortest life due to diffusion of the cathode active species and to increased internal resistance.

A similar series of cells was made with MoCl_5 catholytes (see Table 4).

TABLE 4 TYPICAL ACID-BASE SINGLE CELL TESTS
FOR MoCl_5 CELLS USING A 40 % LiAl ANODE

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	TEMP. & LOAD	NOTES:
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg		
1325	2.43 +	44.5 +	509 +	800 +	31.7 +	44.8	200°	Basic Anolyte Basic Catholyte
1339	2.46 +	45.0 +	488 +	776 +	31.1 +	44.4	&	Acidic Anolyte Basic Catholyte
1338	2.43 +	44.5 +	510 +	809 +	31.4 +	44.9	5	Acidic Anolyte Acidic Catholyte
1328	2.42 +	44.3 +	549 +	802 +	33.7 +	45.0	ohms	Basic Anolyte Acidic Catholyte

As was true for the CuCl_2 cells with 40 % LiAl in the anode, this type of cell (MoCl_5 catholyte with 40 % LiAl anode) has been made before. These cell results were reported earlier for another experiment, Single Cell #1287. A summary of these data is:

$$V_p = 2.35V$$

$$i_p = 43.0 \text{ mA/cm}^2$$

$$t_{80} = 642 \text{ seconds}$$

EARLIER CELLS

$$t_{70} = 876 \text{ seconds}$$

$$ED_{80} = 37.7 \text{ Wh/kg}$$

$$ED_{70} = 47.5 \text{ Wh/kg}$$

Compare this summary to a similar summary about later made cells.

MoCl_5 Cells with 40 % LiAl anode

$$V_p = 2.43V$$

$$i_p = 44.5 \text{ mA/cm}^2$$

$$t_{80} = 509 \text{ seconds}$$

LATER CELLS

$$t_{70} = 800 \text{ seconds}$$

$$ED_{80} = 31.7 \text{ Wh/kg}$$

$$ED_{70} = 44.8 \text{ Wh/kg}$$

These summaries provide a little more of an impression about the magnitude of the variance for single cell test results. This variance was apparently so high that it was necessary to make more cell tests on the four possible types of cells.

For the first series of tests the temperature was held constant at 200°C while the load resistance was varied (see Table 5).

Some of the data from Table 5, the peak voltage and current density, are illustrated with Figure 7. In each of the four sets of data it can be seen that as the current density of a cell is caused to increase the peak voltage is decreased. This is normal behaviour for any cell. It would appear from Figure 7 that at low current density the peak voltages of the four cell types were about the same. However, at the high current densities the cells with basic anolyte were superior to cells with acidic anolytes. This is reasonable. The acidic anolytes have higher internal resistances. Then it would be expected that this would have a greater effect on performance at higher current densities than at lower current densities.

It was hoped that the decrease in performance caused by an increase in the internal resistance of the catholyte would be more than compensated for by an increase due to the increased activity of the cathode active species. From Table 5 it can be seen that, indeed, the cells with acidic catholytes did have superior lifetimes and energy densities. However, this was only readily apparent at the low current densities. Furthermore, the group of control cells, the basic anolyte/basic catholyte cells were also quite good at the low current densities. There was certainly no significant increase in the cell voltage due

TABLE 5 THE EFFECT OF VARIOUS TEST LOADS ON CuCl_2 CELLS
MADE WITH THE FOUR DIFFERENT POSSIBLE COMBINATIONS OF ACIDIC
ANOLYTE, ACIDIC CATHOLYTE, BASIC ANOLYTE AND BASIC CATHOLYTE

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohms	
(1279) (1272)	1.60	180	70	116	12.4	17.7	.81	200°C <hr/> Basic Anolyte <hr/> Basic Catholyte <hr/>
1277	1.73	106	152	268	16.5	25.3	1.5	
1276	1.82	55.5	372	650	22.1	33.8	3	
(1271) (1270)	1.87	34.2	628	1263	23.2	40.1	5	
(1273) (1275)	1.92	13.9	2695	4150	41.2	57.4	12.6	
1278	2.05	7.5	5256	7816	43.8	60.2	25	
1321	1.60	181	82	138	14.5	21.3	.81	200°C <hr/> Basic Anolyte <hr/> Acidic Catholyte
1310	1.90	34.8	781	1440	29.4	47.5	5	
1311	1.96	14.2	2860	-	44.9	-	12.6	
1312	1.97	7.2	6760	8533	54.5	65.0	25	
1307	1.50	169	83	134	12.7	18.1	.81	200°C <hr/> Acidic Anolyte Acidic Catholyte
1306	1.86	34	964	1534	35.0	50.1	5	
1309	1.93	14	3355	-	54.7	-	12.6	
1308	1.95	7	7150	9160	55.9	67.5	25	
1297	1.43	162	44	95	6.05	11.0	.81	Test Temperature 200°C <hr/> Acidic Anolyte <hr/> Basic Catholyte
1301	1.84	56.1	302	407	18.7	23.2	3	
1295	1.87	34.2	593	824	22.2	28.4	5	
1296	1.93	14.0	2338	3023	36.1	43.8	12.6	
1300	1.90	7	6303	7835	48.9	57.3	25	

to use of an acidic catholyte. Perhaps the cathode active species was not significantly activated by the acidic nature of the catholyte or perhaps the catholyte was not as acidic as was believed.

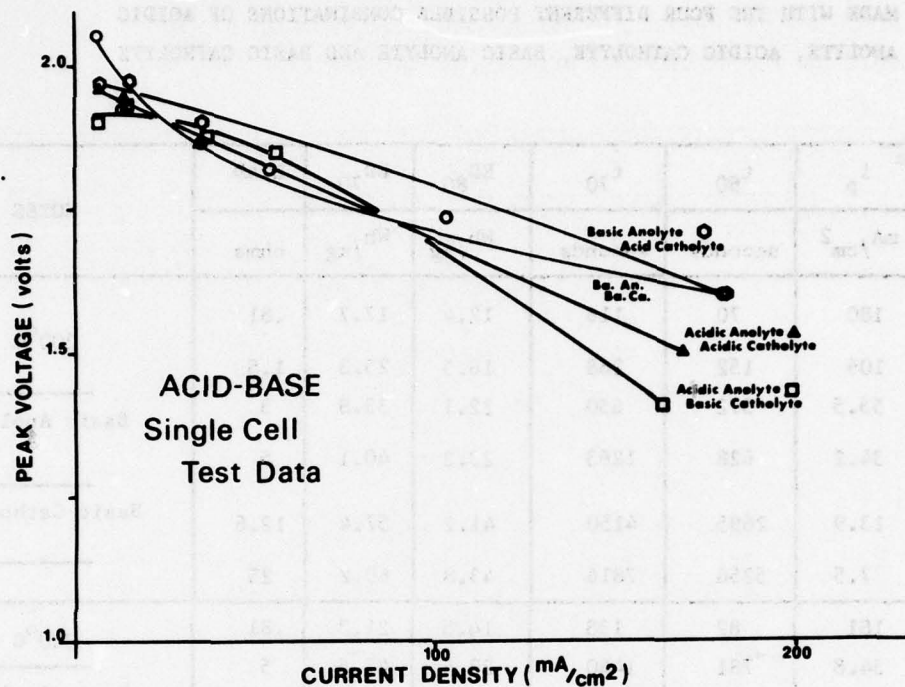


Figure 7. Single Cell Tests Results

The next experiment was to hold the load resistance at 5 ohms and vary the test temperature. These data are tabulated in Table 6.

In three out of four sets of data the peak voltage increased as the temperature increased. The exception was the set of cells made with a basic anolyte and an acidic catholyte.

The lowest voltage recorded was for the lowest temperatures and the cells made with both acidic anolyte and acidic catholyte. These same cells also produced the highest voltage but at the high temperatures. This is somewhat

TABLE 6 THE EFFECT OF VARIOUS TEST TEMPERATURES ON CuCl_2 CELLS
MADE WITH FOUR DIFFERENT POSSIBLE COMBINATIONS OF ACIDIC ANOLYTE,
BASIC ANOLYTE, ACIDIC CATHOLYTE, BASIC CATHOLYTE

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	TEMP.	NOTES
	volts	mA/cm^2	seconds	seconds	mA/cm^2	mA/cm^2	$^{\circ}\text{C}$	
1280	1.89	34.8	763	1233	28.7	41.4	180	5 ohm Load Basic Anolyte Basic Catholyte
(1270)	1.87	34.2	628	1263	23.2	40.1	200	
(1271)	1.88	34.4	665	1100	25.6	37.3	240	
1281	1.89	34.6	595	835	23.4	29.9	280	
1282	1.88	34.4	245	1170	9.36	34.8	300	
1283	1.93	35.3	435	1295	17.2	41.5	320	
1284	1.95	36.7	346	982	14.0	32.5	340	5 ohm Load Basic Anolyte Acidic Catholyte
1319	1.87	34.2	633	1169	22.8	37.1	160	
1320	1.91	34.9	714	1357	26.7	44.6	180	
1310	1.90	34.8	781	1440	29.4	47.5	200	
1322	1.88	34.4	959	1383	35.8	47.3	240	
1324	1.91	34.9	427	1148	16.8	36.8	320	
1313	1.84	33.7	894	1415	31.2	44.6	160	5 ohm Load Acidic Anolyte Acidic Catholyte
1314	1.84	33.7	903	1568	31.7	48.9	180	
1306	1.86	34.0	964	1536	35.0	50.1	200	
1315	1.86	34.0	887	1362	33.0	45.5	240	
1316	1.88	34.4	339	534	13.9	19.2	280	
1317	1.89	34.6	432	1069	16.4	33.8	320	
1318	2.03	37.1	194	672	8.60	23.6	360	5 ohm Load Acidic Anolyte Basic Catholyte
1299	1.86	34.0	608	822	22.6	28.2	180	
1295	1.87	34.2	593	824	22.3	28.4	200	
1303	1.87	34.2	786	1062	30.1	37.5	240	
1304	1.88	34.4	698	972	27.4	34.8	280	
1305	1.94	35.5	613	1137	25.4	40.4	320	

misleading because there was a tendency to form a "spike" in the activation curve when the test temperature was over 300°C. Actually there was very little difference in the peak voltages produced. Table 7 is a tabulation of average peak voltage and standard deviation for the data for each cell type in Table 6.

TABLE 7 AVERAGE VOLTAGE, STANDARD DEVIATION
AND 1 σ BANDS FOR THE FOUR DATA SETS IN TABLE 5

CELL TYPE	AVERAGE VOLTAGE	STANDARD DEVIATION	1 BAND
Basic Anolyte Basic Catholyte	1.8975	0.0276	1.925 1.870
Basic Anolyte Acidic Catholyte	1.8940	0.0182	1.912 1.876
Acidic Anolyte Acidic Catholyte	1.8857	0.0663	1.952 1.819
Acidic Anolyte Basic Catholyte	1.884	0.0321	1.916 1.852

It is reasonable to explain the low voltage for the acidic anolyte/acidic catholyte cells at low temperature due to increased melting point and decreased conductivity of the electrolyte. No explanation is offered for the tendency to form an activation spike at higher temperature or in an acidic catholyte.

The biggest difference expected in acidic and basic electrolytes was in internal resistance. Tables 8, 9, & 10 tabulate the internal resistance data that were accumulated during the tests described in Tables 3, 5, and 6. It was

expected that the acidic electrolytes would cause their cells to have high internal resistances. However, this was not always the case. For example, in Table 9 the group of cells which displayed the least internal resistance was the group with the acidic anolyte and basic catholyte. There is no immediate explanation for why this group has a lower internal resistance. The control group, with a basic anolyte and a basic catholyte, was predicted to have the lowest internal resistance. Also, the internal resistance always increased as more current passed. The effect was about as great for low current density situations as for high current density cells. Finally, there is no reason for why the internal resistance increased with temperature.

TABLE 8 INTERNAL RESISTANCE FOR TYPICAL CELLS OF EACH OF THE FOUR TYPES TESTED

S/N	V _p	t ₈₀	load	Temp.	Spec. r at t ₀	Spec. r at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	seconds	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1294	1.87	551	5	200	.30	1.3	4.8	6.7	Basic Anolyte Basic Catholyte
1295	1.87	593	5	200	.90	1.6	3.0	7.6	Acidic Anolyte Basic Catholyte
1306	1.86	964	5	200	.98	1.1	4.5	10.6	Acidic Anolyte Acidic Catholyte
1310	1.90	781	5	200	1.2	4.8	10.1	X	Basic Anolyte Acidic Catholyte

TABLE 9 INTERNAL RESISTANCE FOR CuCl_2 CELLS OF
EACH OF THE FOUR TYPES TESTED WITH CONSTANT TEM-
PERATURE AND A VARIABLE LOAD.

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES:
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
(1272) (1279)	1.60	71	.81	200	1.5	2.9	3.1	X	Basic Anolyte Basic Catholyte Control Group
(1270) (1271)	1.87	628	5	200	.75	3.1	5.7	21.5	
(1273) (1275)	1.92	2695	12.6	200	.55	.80	8.1	14.4	
1278	2.05	5256	25	200	.35	X	X	X	
1321	1.60	82	.81	200	1.3	1.8	3.1	4.1	Basic Anolyte Acidic Catholyte
1310	1.90	781	5	200	1.2	4.8	10.1	X	
1311	1.96	2860	12.6	200	.73	X	9.0	X	
1312	1.97	6760	25	200	.36	X	X	X	
1307	1.50	83	.81	200	X	1.5	3.8	5.4	Acidic Anolyte Acidic Catholyte
1306	1.86	964	5	200	.98	1.1	4.5	10.6	
1309	1.93	3355	12.6	200	3.7	4.9	10	16.7	
1308	1.95	7150	25	200	1.4	1.6	17.7	41.9	
1297	1.43	44	.81	200	X	3.0	9.7	X	Acidic Anolyte Basic Catholyte
1295	1.87	593	5	200	.90	1.6	3.0	7.6	
1296	1.93	2338	12.6	200	.29	.31	2.8	4.0	
1300	1.90	6303	25	200	.29	.32	.70	6.6	

TABLE 10 INTERNAL RESISTANCE FOR CuCl_2 CELLS OF EACH OF THE FOUR TYPES TESTED WITH CONSTANT LOAD RESISTANCE AND A VARIABLE TEST TEMPERATURE.

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES:
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1280	1.89	763	5	180	1.2	2.0	4.0	X	Basic Anolyte Basic Catholyte Control Group
1281	1.88	665	5	240	.30	2.0	5.5	X	
1283	1.88	245	5	300	.30	6.0	11.3	12.5	
1285	1.95	346	5	340	.14	3.8	9.9	X	
1320	1.91	714	5	180	1.2	3.5	5.0	10.7	Basic Anolyte Acidic Catholyte
1322	1.88	959	5	240	.29	2.0	5.5	12.9	
1324	1.91	427	5	320	.29	5.6	10.7	13.0	
1314	1.84	903	5	180	2.7	3.6	5.5	12.3	Acidic Anolyte Acidic Catholyte
1315	1.86	887	5	240	.29	2.6	6.7	13	
1317	1.89	432	5	320	.29	5.9	11.9	16.1	
1318	2.03	194	5	360	2.2	X	10.1	19.8	
1299	1.86	608	5	180	.29	2.3	3.3	5.5	Acidic Anolyte Basic Catholyte
1303	1.87	786	5	240	.29	1.3	3.3	7.8	
1304	1.88	698	5	280	.29	1.6	5.8	11.3	
1305	1.94	613	5	320	.57	4.1	10.2	12.8	

Similar sets of data were collected for MoCl_5 cells with 40 % LiAl anodes. These cells were very disappointing because there were very few noticeable differences in the acid-base electrolytes. Tables 11, 12, and 13 tabulate the internal resistance data for these cells. Once again there is no noticeable difference in the internal resistance of the four types of cells.

Looking at Tables 10, 11, and 12 it is interesting to notice the change in the internal resistance as the cell is discharged. For a CuCl_2 cell the internal resistance always started out low and gradually increased. The MoCl_5 cells start out with relatively high internal resistances which drops to a minimum value. Then, after hitting the minimum the internal resistance will start to gradually climb again. This pattern has been noted for the internal resistance of all LiAl/MoCl_5 cells made before. The only differences are the times when the minimum is reached. For example, the minimum occurred about t_{90} for cell #1325 but it occurred sometime after t_{70} for cell #1328 (Table 11). Once again, no real effect can be assigned to any particular combination of acidic or basic electrolyte.

TABLE 11 INTERNAL RESISTANCES OF MoCl_5 CELLS
OF EACH OF THE FOUR DIFFERENT TYPES

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES:
	volts	seconds	ohms	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1325	2.43	509	5	200	.70	.25	.28	.66	Basic Anolyte Basic Catholyte
1328	2.42	549	5	200	.93	.76	.56	.32	Basic Anolyte Acidic Catholyte
1338	2.43	510	5	200	.90	.25	.29	.33	Acidic Anolyte Acidic Catholyte
1339	2.46	488	5	200	2.1	.76	.28	.32	Acidic Anolyte Basic Catholyte

TABLE 12 THE EFFECT OF VARIOUS CURRENT DENSITIES ON
MoCl₅ CELLS AT CONSTANT TEMPERATURE AND WITH THE FOUR
POSSIBLE ACID-BASE TYPES

S/N	V _p	t ₈₀	load	Temp.	Spec. r at t ₀	Spec. r at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	seconds	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1326	1.91	86	.81	200	1.1	1.5	.93	1.4	Basic Anolyte Basic Catholyte
1325	2.43	509	5	200	.70	.25	.28	.66	
1327	2.51	928	12.6	200	.55	1.2	.69	.79	
1329	1.96	91	.81	200	1.1	1.3	.96	1.3	Basic Anolyte Acidic Catholyte
1328	2.42	549	5	200	.93	.76	.56	.32	
1332	2.56	954	12.6	200	1.1	.60	.68	.77	
13X			.81						Acidic Anolyte Acidic Catholyte
1338	2.43	510	5	200	.90	.25	.29	.33	
X			12.6						
X			.81						Acidic Anolyte Basic Catholyte
1339	2.46	488	5	200	2.1	.76	.28	.32	
X			12.6						

TABLE 13 THE EFFECT OF VARIOUS TEST TEMPERATURES AT
CONSTANT LOAD FOR MoCl₅ CELL WITH A 40 % LiAl ANODE
AND A BASIC ANOLYTE AND ACIDIC CATHOLYTE

S/N	V _p	t ₈₀	load	Temp.	Spec. r at t ₀	Spec. r at t ₉₀	Spec. r at t ₈₀	Spec. r at t ₇₀	NOTES
	volts	seconds	ohms	°C	ohm·cm ²	ohm·cm ²	ohm·cm ²	ohm·cm ²	
1334	2.46	349	5	160	1.8	2.3	2.0	.96	Basic Anolyte
1335	2.51	387	5	180	1.3	.49	.82	.94	
1328	2.42	549	5	200	.93	.76	.56	.32	
1333	2.46	469	5	240	.23	.25	.56	1.3	Acidic Catholyte
1336	2.52	165	5	280	.23	.25	.55	.32	
1337	2.55	123	5	320	.23	.24	.27	.63	

It was felt that the lack of dramatic effects due to the use of acidic electrolyte may have been due to the fact that the electrolyte was not as acidic as was believed. Some NaAlCl_4 was purchased from Alcoa Aluminum containing 69 ^m/o AlCl_3 . This material was ground until it could pass through a #40 sieve and was mixed with 10 ^w/o Cab-O-Sil. The mixtures were then heated to 250°C in a covered vessel in the argon box. The fused mix was then ground until it would all pass through a #40 sieve. It was felt that perhaps the excess AlCl_3 was all lost during the overnight heating at 250°C and that maybe the acid mixtures were no longer acidic.

For this reason it was decided to mix binder into the NaAlCl_4 mechanically instead of fusing it in. Since Cab-O-Sil does not mix well with salt mixtures at room temperature it was decided to use kaolin. So, a 40 ^w/o mixture of kaolin was mixed in ground NaAlCl_4 (69 ^w/o AlCl_3) by stirring and tumbling. The mixture was never heated and the mixing was done in the argon box so that none of the excess AlCl_3 could be lost. These electrolytes were surely acidic (A #1044, A #1046, C #1079).

Some basic electrolyte (49.8 ^w/o AlCl_3) was made with kaolin so that all four types of cells could be made with kaolin containing electrolytes. Table 14 displays the results of representative cells at 200°C and 5 ohm loads.

	1	2	3	4	5	6	7	8	9
Cell Type	1	2	3	4	5	6	7	8	9
Electrolyte	1	2	3	4	5	6	7	8	9
Temperature	1	2	3	4	5	6	7	8	9
Current	1	2	3	4	5	6	7	8	9
Voltage	1	2	3	4	5	6	7	8	9
Efficiency	1	2	3	4	5	6	7	8	9
Life	1	2	3	4	5	6	7	8	9
Notes	1	2	3	4	5	6	7	8	9

TABLE 14 TYPICAL SINGLE CELL TEST RESULTS FOR CuCl_2
CELLS MADE WITH THE FOUR POSSIBLE COMBINATIONS OF
ACIDIC ELECTROLYTE MIXED WITH KAOLIN

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	
1355	2.03	37.1	603	1174	25.2	43.2	Basic Anolyte Basic Catholyte
1347	1.84	33.7	674	1294	23.2	39.2	Acidic Anolyte Basic Catholyte
1344	1.74	31.8	363	601	11.3	16.8	Acidic Anolyte Acidic Catholyte
1340	1.81	33.1	895	1379	30.9	43.0	Basic Anolyte Acidic Catholyte

Since the cells with the basic anolyte and the acidic catholyte were the best (as had been hoped) more cells were made like these and tested at constant temperature.

TABLE 15 TYPICAL SINGLE CELL TEST RESULTS FOR CELLS
MADE WITH CuCl_2 , AN ACIDIC CATHOLYTE, A BASIC CATHOLYTE,
AND USING KAOLIN FOR A BINDER. THE TEST TEMPERATURE WAS
200°C

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀		NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	load	
1343	1.43	162	59	105	7.97	12.4	.81	Basic Anolyte Acidic Catholyte 200°C
1340	1.81	33.1	895	1379	30.9	43.0	5	
1342	1.91	13.9	2375	3250	35.8	45.5	12.6	
1341	1.94	7.1	6950	8460	52.3	60.9	25	

When the results in Table 3 are compared to the results in Table 14 it is actually a comparison of the suspect heated electrolytes with the nonsuspect electrolytes mechanically mixed with kaolin. The first impression formed while making this comparison is that the cells with Cab-O-Sil (Table 3) were, overall, better than the cells with kaolin. This was anticipated as a result of the kaolin containing cells reported prior to this experiment. Furthermore, it appears that many of the properties that were expected to be found in Table 3 did appear in Table 14. For example, the best cell was #1340 which had an acidic catholyte and a basic anolyte. The worst cell was #1344 which was made with both acidic anolyte and acidic catholyte.

Another good comparison of the heated electrolytes and the mechanically mixed electrolytes is Table 9 with Table 16.

TABLE 16 INTERNAL RESISTANCE RESULTS FOR CELLS
MADE WITH CuCl_2 CATHODES, 40 % ANODES, AND ELECTROLYTES WITH MECHANICALLY MIXED KAOLIN FOR A BINDER.

S/N	V_p	t_{80}	load	Temp.	Spec. r at t_0	Spec. r at t_{90}	Spec. r at t_{80}	Spec. r at t_{70}	NOTES
	volts	seconds	ohm	$^{\circ}\text{C}$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	$\text{ohm}\cdot\text{cm}^2$	
1355	2.03	603	5	200	.82	2.7	.68	4.3	Basic Anolyte Basic Catholyte
1347	1.84	674	5	200	1.8	3.0	4.1	8.1	Acidic Anolyte Basic Catholyte
1344	1.74	363	5	200	2.4	3.1	3.7	5.1	Acidic Anolyte Acidic Catholyte
1340	1.81	895	5	200	1.8	3.4	6.5	11.7	Basic Anolyte Acidic Catholyte
1343	1.43	59	.81	200	1.5	2.4	3.7	5.2	Basic Anolyte Acidic Catholyte 200 $^{\circ}\text{C}$
1340	1.81	895	5	200	1.8	3.4	6.5	11.7	
1342	1.91	2375	12.6	200	.73	4.8	9.9	24.9	
1341	1.94	6950	25	200	.36	X	14.1	46.2	

This comparison shows that the internal resistance of the kaolin cells is higher than the internal resistance of the Cab-O-Sil cells. This was also expected as a result of the work done prior to this experiment.

There was one other large difference in the heated and mechanically mixed electrolytes. When the tested cells were examined, post mortem, "air bubble" spaces were found in the mechanically mixed cells but not in the heated cells. This could be because most of the excess AlCl_3 had been lost in the heated electrolytes and very little was lost in the mechanically mixed electrolytes. Therefore, it is logical to believe that either the effect of the acidic electrolytes is not as great as was originally expected, or the full effect of the acidic electrolytes can be achieved with just a slight excess of AlCl_3 . That is, it appears that an electrolyte with a composition of 50.2 m/o AlCl_3 can be just as effective as an electrolyte with 69 m/o AlCl_3 and the disadvantage of the volatile AlCl_3 will be much less.

One further observation needs to be made about the acid-base experiments. At first glance it would appear that the acidic electrolytes have very little effect on cell performance. But, there is dramatic evidence that the acidic electrolytes can produce a significantly superior cell. See Figure 25 in the conclusion section of this report, p.93. From Figure 25 it can be seen that the use of acidic electrolytes has produced superior cells with about a 20% increase in energy density.

SUMMARY & CONCLUSION

Some NaAlCl_4 containing 69 m/o AlCl_3 has been received from Alcoa Aluminum. This material was fused at 250°C and mixed with Cab-O-Sil to produce an acidic anolyte. A portion of this acidic anolyte was mixed with CuCl_2 (or MoCl_5)

to produce an acidic catholyte. Using both acidic and basic anolytes and catholytes the four possible types of cells were constructed and tested. Later, it was suspected that the excess AlCl_3 was volatilized out of the NaAlCl_4 during the fusing process so new acidic electrolytes were prepared by mechanically mixing the NaAlCl_4 with 40 % kaolin powder. The four types of cells were duplicated and tested. Some of the specific properties of these cells were vague and confusing but the general conclusion that acidic electrolytes can make superior cells was demonstrated.

SECTION IX

ALTERNATE CATHODE CHLORIDES

Most of the cell results reported so far have been MoCl_5 cells. Seiler Research Laboratory at the Air Force Academy has recently published work which strongly suggests that some other cathode chlorides may produce even better cells than MoCl_5 .^{5,6} Three such alternate cathode chlorides have been tested; iron(III) chloride, FeCl_3 , copper(II) chloride, CuCl_2 , and tungsten(VI) chloride, WCl_6 .

5. Reference. J. C. Nardi, J. K. Erbacher, C. L. Hussey, "High Energy Density Pelletized Aluminum Chloride Thermal Batteries; Part II Cathode Screening," FJSRL-TR-77-0004, April, 1977.
6. Reference. J. K. Erbacher, C. L. Hussey, L. A. King, "The Discharge Behaviour of a $\text{LiAl}/\text{NaAlCl}_4/\text{CuCl}_2$ Pelletized Thermal Cell."

Quite a large number of catholytes had to be prepared to test these materials. Most of these catholytes were regular test catholytes:

56 gms cathode chloride

26 gms anolyte

18 gms graphite

There were a few exceptions to this formula and these will be noted when necessary.

The first chloride tested was FeCl_3 . A test catholyte was made with FeCl_3 and a DSC spectrum was generated for this material. This DSC spectrum was interesting. The first feature was a large exotherm which started at about 147°C and peaked at 169°C . There were no "moisture" peaks at 100°C such as may be expected in a MoCl_5 catholyte spectrum. The second feature was a broad endotherm which started to form at about 311°C . When the sample reached 327°C it was cooled back to 47°C and reheated. The only feature on the reheated spectrum was a small endotherm at about 149°C .

As the FeCl_3 testing progressed it was decided to make a catholyte which contained both FeCl_3 and MoCl_5 . For this purpose a test catholyte was made with MoCl_5 . This MoCl_5 catholyte was then mixed, 50:50, with the FeCl_3 catholyte to make a $\text{MoCl}_5/\text{FeCl}_3$ catholyte.

The DSC spectrum of the MoCl_5 catholyte was quite typical of a MoCl_5 catholyte with a large "moisture" peak of 107°C . This was followed by an exotherm which peaked at 145°C , and endotherm at 159°C and another endotherm at 181°C . The general shape of this spectrum was recognizable as a MoCl_5 catholyte except that it was generally more exothermic in the area between 107°C and 145°C . Upon cooling and reheating this sample, the baseline becomes flat with constant slope and with only three features - a large endotherm at 141°C , a small exotherm at 180°C , and a medium sized endotherm at 255°C .

When the above two catholytes were combined to make the $\text{MoCl}_5/\text{FeCl}_3$ catholyte a different DSC spectrum was generated. The two endotherms characteristic of a MoCl_5 catholyte were still present (103°C and 157°C). These were followed by an exotherm at 187°C and two other exotherms at 269°C and 275°C . These latter two exotherms were too close to be completely resolved. Upon cooling and reheating this sample the only feature was an endotherm at 167°C .

It is noted that in each of the three spectra described above the combined area under the peaks in the reheated region of the spectra was much smaller than the combined area of the peaks in the spectra when the samples were heated the first time. This suggests that the catholytes may be more thermally manageable if they are fused, ground, and sieved before making into cells. This practice is not uncommon in the thermal battery industry for anolytes but is usually not done for catholytes. The procedure has been anticipated in R & D Test Plan, Item 1.15, Prefuse Catholyte.

These two FeCl_3 catholytes have been tested in 22 single cell tests. These tests are organized into four groups:

- 1) FeCl_3 catholyte with 20 w/o LiAl alloy
- 2) $\text{FeCl}_3/\text{MoCl}_5$ catholyte with 20 w/o LiAl alloy
- 3) FeCl_3 catholyte with Anode #7*
- 4) $\text{FeCl}_3/\text{MoCl}_5$ catholyte with Anode #7*

Anode #7 contains only half as much LiAl as the 20 w/o LiAl alloy. This was used because this anode produces a smaller activation, high voltage peak than pure alloy.

The following is a tabulation of single cell results for a cell made from FeCl_3 catholyte with an anode of 20 w/o LiAl alloy.

* Anode #7 is a mixture of 50% Al powder and 50% LiAl alloy (20 w/o). This will be discussed in more detail later in this report.

TABLE 17 FeCl_3 & 20 W/o LiAl

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	LOAD
1162	1.50	169	89	107	14.5	16.4	.81
1161	1.75	107	151	185	17.8	20.4	1.5
1160	2.02	61.6	290	381	22.6	27.3	3
1159	2.18	39.9	322	424	16.8	20.5	5
1163	2.25	16.3	625	828	14.2	18.8	12.6
1164	2.24	8.2	736	1143	8.34	11.5	25

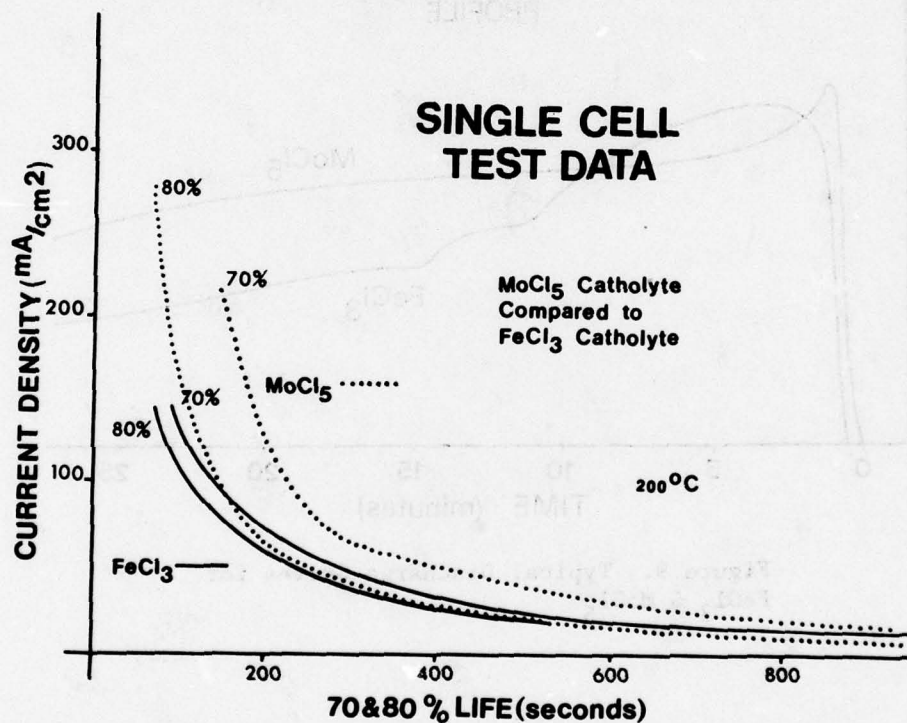


Figure 8. Single Cell Test Results which compare FeCl_3 with MoCl_5

Figure 8 charts current density vs. 80 & 70% lifetime. Examining these curves it can be seen that, for the 80% life, the FeCl_3 compares very closely to MoCl_5 at the lower current densities but at the higher current densities the FeCl_3 is inferior to the MoCl_5 . When the lifetime is measured to 70% of peak the FeCl_3 is entirely inferior to MoCl_5 . This is because the FeCl_3 loses potential very quickly in the 75% to 50% range. This is illustrated in Figure 9 which is a drawing of two typical discharge curves - one each for MoCl_5 and FeCl_3 .

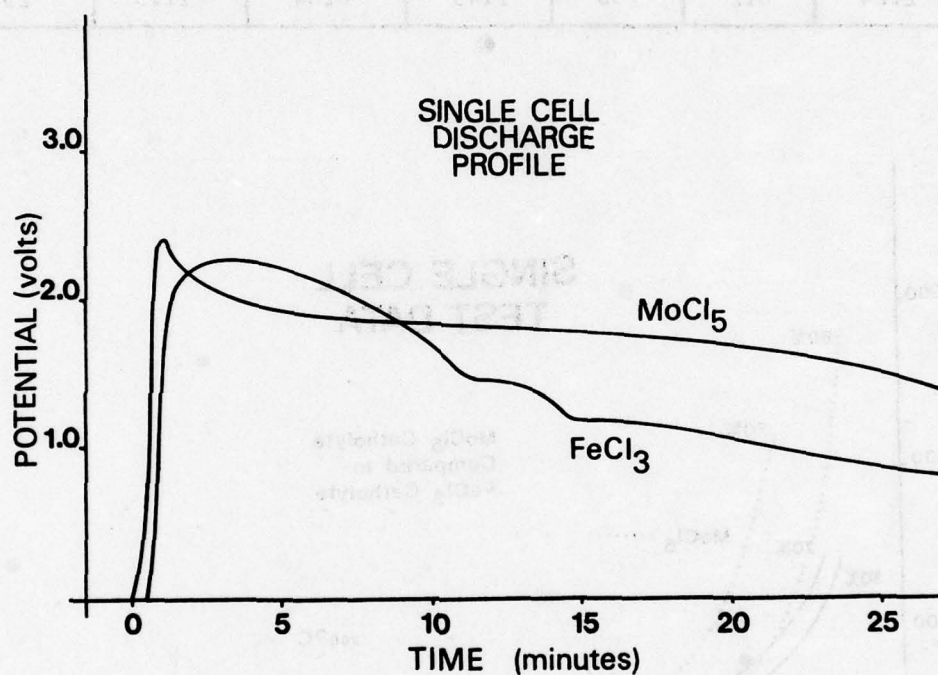


Figure 9. Typical Discharge Curves for FeCl_3 & MoCl_5

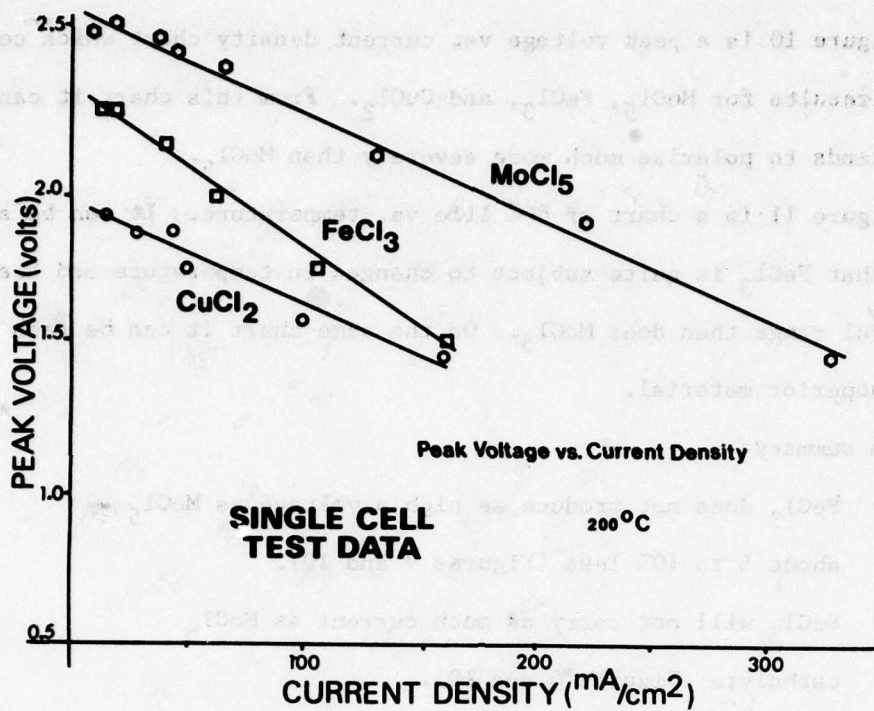


Figure 10. Peak Voltage vs. Current Density Comparisons for MoCl_5 , CuCl_2 , and FeCl_3

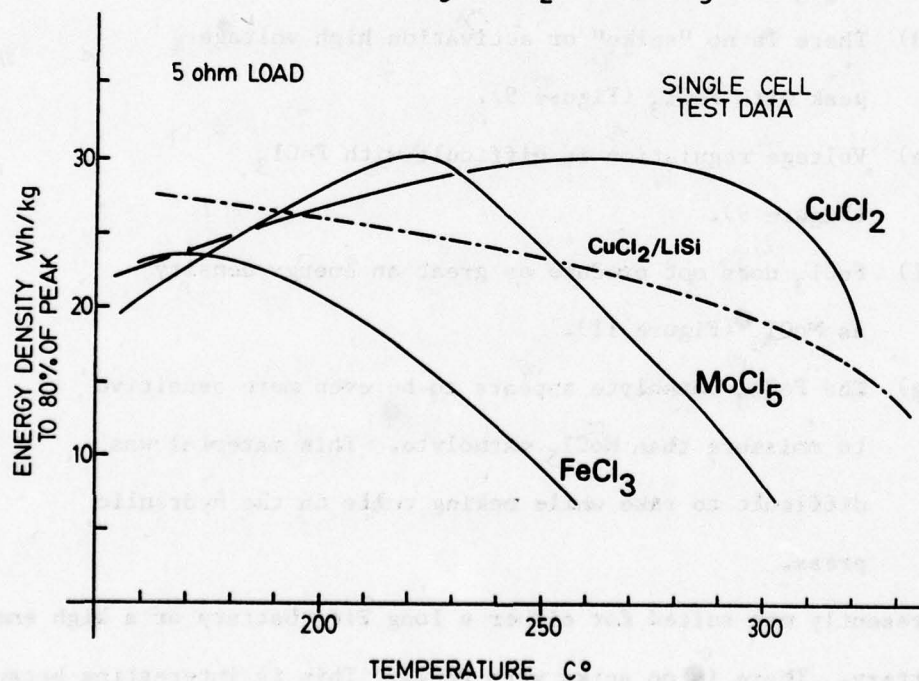


Figure 11. A Comparison of Temperature Tolerance for FeCl_3 , CuCl_2 , and MoCl_5

Figure 10 is a peak voltage vs. current density chart which compares single cell results for MoCl_5 , FeCl_3 , and CuCl_2 . From this chart it can be seen that FeCl_3 tends to polarize much more severely than MoCl_5 .

Figure 11 is a chart of 80% life vs. temperature. It can be seen from this chart that FeCl_3 is quite subject to changes in temperature and has a much smaller useful range than does MoCl_5 . On the same chart it can be seen that CuCl_2 is a superior material.

In summary:

- a) FeCl_3 does not produce as high a voltage as MoCl_5 — about 5 to 10% less (Figures 9 and 10).
- b) FeCl_3 will not carry as much current as MoCl_5 catholyte (Figures 8 and 10).
- c) FeCl_3 is much more temperature sensitive than MoCl_5 (Figure 11).
- d) There is no "spike" or activation high voltage peak with FeCl_3 (Figure 9).
- e) Voltage regulation is difficult with FeCl_3 (Figure 9).
- f) FeCl_3 does not produce as great an energy density as MoCl_5 (Figure 11).
- g) The FeCl_3 catholyte appears to be even more sensitive to moisture than MoCl_5 catholyte. This material was difficult to rake while making cells on the hydraulic press.

FeCl_3 is presently not suited for either a long life battery or a high energy density battery. There is no spike with FeCl_3 . This is interesting because it

has not been known whether the spike formed as a result of a reaction between the anode and anolyte or as a reaction at the cathode. The anode was not changed for these FeCl_3 cells but the spike disappeared. This certainly suggests that the spike is associated with the cathode and not the anode.

It was noticed that in the first few moments of life the FeCl_3 had a better discharge profile than MoCl_5 , (Figure 9). This suggested that the MoCl_5 discharge curve could be straightened by mixing FeCl_3 into the catholyte. This was tried with catholyte C #1043.

Table 18 is a tabulation of all of the single cell results with this mixed $\text{MoCl}_5/\text{FeCl}_3$ catholyte.

TABLE 18 SINGLE CELL RESULTS WITH $\text{MoCl}_5/\text{FeCl}_3$
CATHOLYTE AND EITHER, 20 w/o or ANODE #7

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	LOAD	NOTES
-	volts	mA	seconds	seconds	WH/kg	WH/kg	C°	ohms	-
1177	1.82	206	120	176	27.6	35.7	200	.81	C #1043 & 20 w/o
1176	2.40	43.9	470	612	28.4	34.6	200	5	C #1043 & 20 w/o
1178	2.54	18.4	886	1236	23.3	30.1	200	12.6	C #1043 & 20 w/o
1179	2.70	49.4	19	69	5.26	12.3	160	5	C #1043 & 20 w/o
1180	2.36	43.1	495	715	28.2	37.5	180	5	C #1043 & 20 w/o
1174	1.79	202	109	146	25.0	28.7	200	.81	C #1043 & An #7
1173	2.31	42.3	436	565	24.5	27.7	200	5	C #1043 & An #7
1175	2.40	17.4	754	952	18.3	21.7	200	12.6	C #1043 & An #7

Catholyte #1043 did appear to help raise the discharge curve of an AlLiMo cell. Figure 12 is a sketch of a "typical $\text{MoCl}_5/\text{FeCl}_3$ cell discharge and a typical MoCl_5 cell discharge". The spike was not particularly affected as can be seen by the potential of 2.70 volts for cell #1179. The energy density for the higher current densities was not as good for $\text{MoCl}_5/\text{FeCl}_2$ as for MoCl_5 alone.

It is also noteworthy that for C #1037, the FeCl_3 catholyte, the cells all displayed an ohmic resistance (internal iR drop) which was an order of magnitude greater than for the MoCl_5 cells. When the FeCl_3 catholyte was mixed with the MoCl_5 catholyte to obtain C #1043 the cells displayed an iR drop more characteristic of a MoCl_5 cell than a FeCl_3 cell. Furthermore the iR drop in the FeCl_3 cells increased dramatically as the cell was discharged. Table 19 is a tabulation of some examples of the behaviour of the iR drop for FeCl_3 cells compared to $\text{MoCl}_5/\text{FeCl}_3$ cells.

In summary the FeCl_3 cells appear to have a greater internal resistance than other cells tested so far. It should also be noted that this is only the first attempt to make cells with anything except MoCl_5 . These alternate cells are certainly not optimized. Some of the noted features of these systems may change dramatically with something as simple as a cell formula change. Only further experimentation will reveal these features and therefore, any conclusions concerning the use of these materials must be considered preliminary or initial and not final.

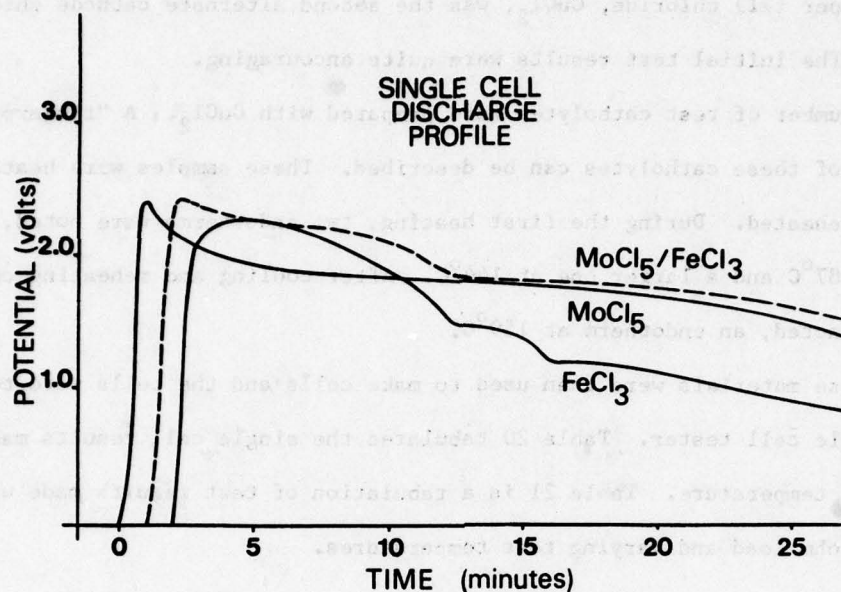


Figure 12. Single Cell Discharge Profiles
for a $\text{MoCl}_5/\text{FeCl}_3$ type Cell

TABLE 19 SPECIFIC RESISTIVITIES OF
VARIOUS CELLS COMPARED

S/N	T	Load	SP.R. $R_{\text{INT}100}$	SP.R. $R_{\text{INT}90}$	SP.R. $R_{\text{INT}80}$	SP.R. $R_{\text{INT}70}$	NOTES
	$^{\circ}\text{C}$	ohms	$\text{ohm}\cdot\text{cm}^2$ at Peak	$\text{ohm}\cdot\text{cm}^2$ at 90%	$\text{ohm}\cdot\text{cm}^2$ at 80%	$\text{ohm}\cdot\text{cm}^2$ at 70%	
1028	200	5	2.33	1.26	0.85	0.64	MoCl_5 Cells
1029	200	1.5	2.39	1.26	1.24	1.51	1001 - 1006
R_{INT} AT LOWEST MEASURABLE LIMIT WITH EXISTING EQUIPMENT - $R_{\text{INT}} = 1.5$							MoCl_5 Cells with LiCl 1056 - 1087 FeS_2 Cells 1008 - 1113
1160	200	3	4.42	3.68	3.81	5.26	FeCl_3 Cells 1159 - 1172
1165	160	5	8.17	5.93	6.83	-	
1166	180	5	9.15	5.62	5.64	-	
1170	200	5	2.55	2.52	6.39	3.62	
1173	200	5	.719	.264	.597	-	$\text{MoCl}_3/\text{FeCl}_3$ Cells 1173 - 1180
1175	200	12.6	.289	.324	.721	-	

Copper (II) chloride, CuCl_2 , was the second alternate cathode chloride considered. The initial test results were quite encouraging.

A number of test catholytes were prepared with CuCl_2 . A "fingerprint" DSC spectrum of these catholytes can be described. These samples were heated, cooled, and reheated. During the first heating, two endotherms were noted, a small one at 87°C and a larger one at 144°C . After cooling and reheating only one peak was noted, an endotherm at 159°C .

These materials were then used to make cells and the cells were tested with the single cell tester. Table 20 tabulates the single cell results made at constant test temperature. Table 21 is a tabulation of test results made with a constant 5 ohm load and varying test temperatures.

TABLE 20 TABULATION OF CuCl_2
SINGLE CELL RESULTS

S/N	V_p	i_p	t_{80}	t_{70}	ED_{80}	ED_{70}	T	LOAD	NOTES
-	volts	mA	seconds	seconds	WH/kg	WH/kg	$^\circ\text{C}$	ohms	-
1182	1.45	164	97	153	14.0	20.0	200	.81	CuCl_2 Catholyte
1186	1.67	102	184	327	18.6	28.8	200	1.5	CuCl_2 Catholyte
1185	1.76	53.7	365	687	20.1	32.8	200	3	CuCl_2 Catholyte
1181	1.88	44.2	727	1469	26.3	46.3	200	5	CuCl_2 Catholyte
1184	1.85	28.2	1095	1805	32.1	63.0	200	6	CuCl_2 Catholyte
1183	1.93	14	379	2633	39.5	57.3	200	12.6	CuCl_2 Catholyte

From Table 20 it can be seen that the voltage for CuCl_2 cells are generally lower than for either MoCl_5 or FeCl_3 . Despite this handicap the energy density to 80 and 70% of peak is excellent. This is because the discharge curve is so straight (see Figure 13). The internal resistance of these cells was comparable to MoCl_5 cells.

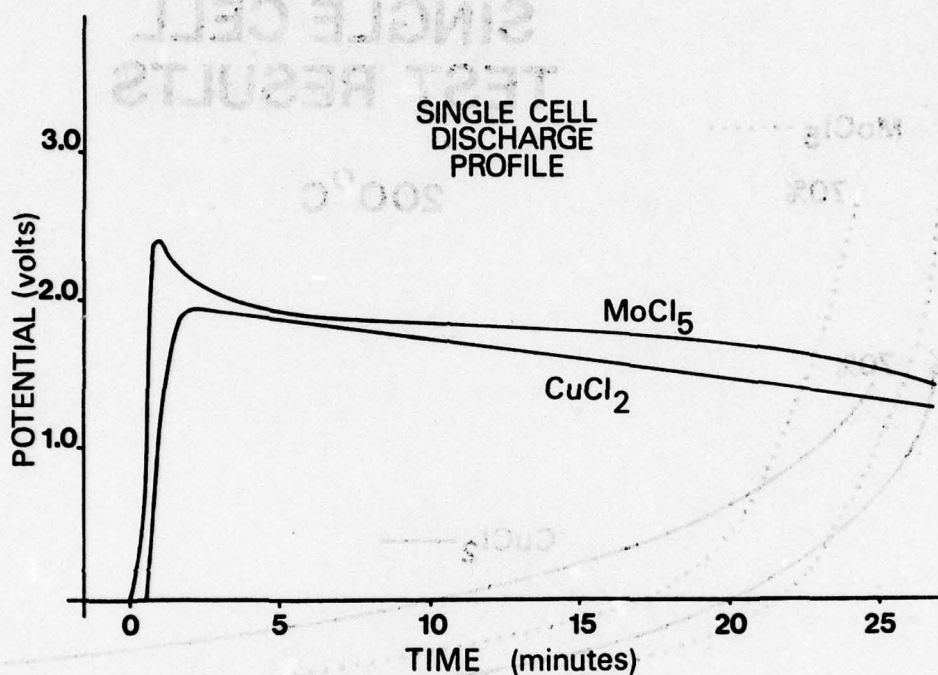


Figure 13. A Typical CuCl_2 Single Cell Discharge Curve Compared to a Typical MoCl_5 Discharge Curve

Figure 14 shows how the current density vs. lifetime curve compares with the MoCl_5 system. The conclusion is the CuCl_2 is at least equal to and is even superior to MoCl_5 at the lower current densities.

CuCl_2 cells were also tested at various temperatures. Figure 11 (see Table 21) is a graph of data points from single cell tests #1261 to #1269. The purpose of this figure is to show the superior temperature tolerance of the CuCl_2 catholyte. This is a large advantage for the CuCl_2 system.

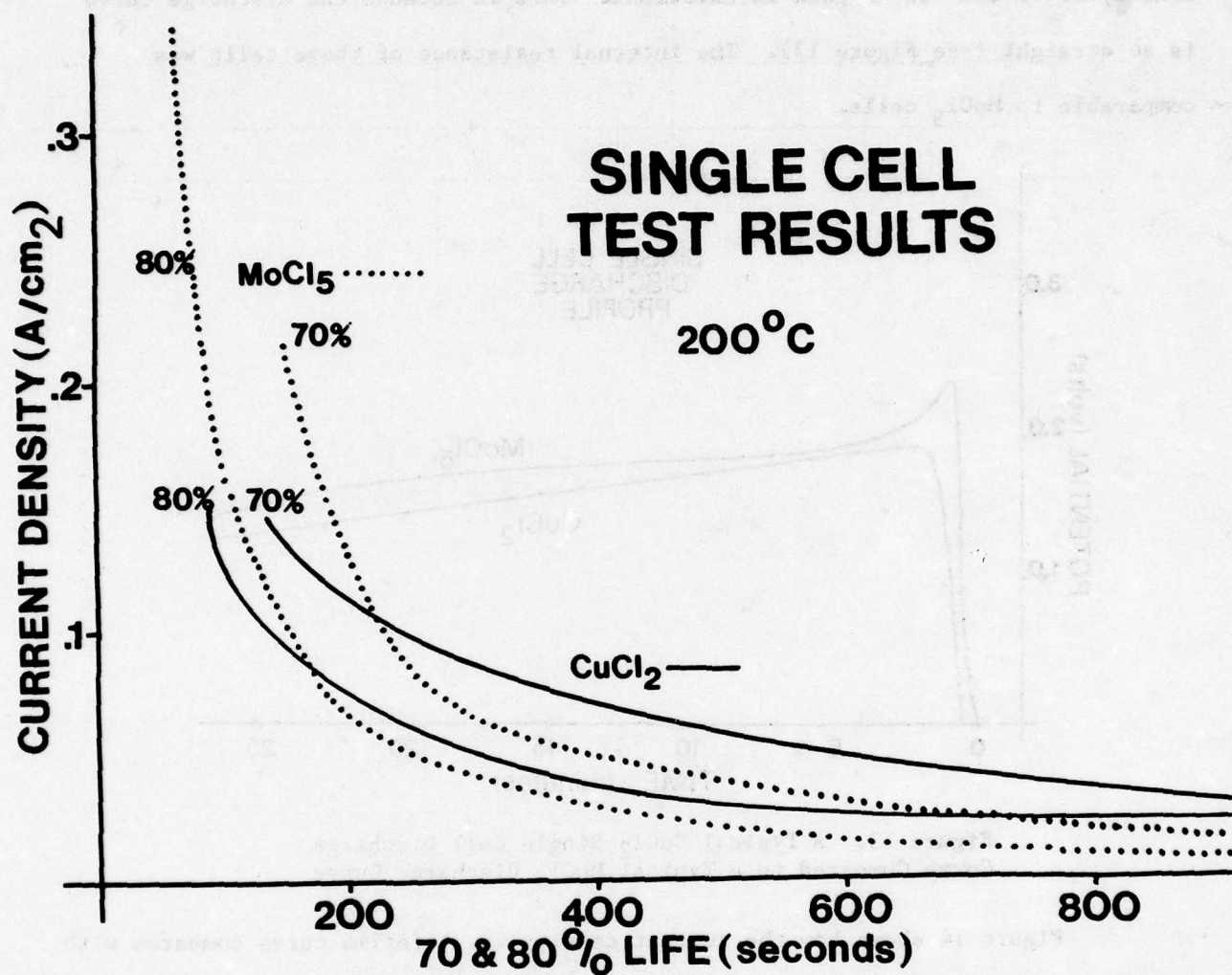


Figure 14. CuCl₂ is Superior to MoCl₅
at the Low Current Densities

TABLE 21 CuCl_2 SINGLE CELL TEST RESULTS

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	T	NOTES
-	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	°C	-
1261	1.86	34	715	126	25.9	40.4	160	Test Load
1262	1.86	34	759	1180	27.5	38.6	180	
1263	1.83	33.5	635	940	22.5	30.3	200	
1264	1.85	33.9	694	1172	25.2	37.7	220	5 ohms
1265	1.85	33.9	895	1203	32.9	40.9	240	
1266	1.87	34.2	619	896	23.5	30.9	260	
1267	1.87	34.2	771	1141	30.1	40.0	280	
1263	1.88	32.1	839	1286	32.2	44.2	300	
1269	1.91	34.9	538	1073	21.3	36.2	320	

CuCl_2 cells were also tested with a LiSi anode. These results will be discussed later in the "Alternate Anode" section of this report.

In conclusion, the CuCl_2 testing done so far demonstrates that the CuCl_2 is capable of producing energy at least as well as the MoCl_5 system with the additional advantages of greater temperature tolerance and greater moisture tolerance. There is the disadvantage of lower voltage with CuCl_2 cells.

It was concluded previously that FeCl_3 was not a desirable cathode material. However, FeCl_3 does have a higher peak voltage than CuCl_2 . Mostly for this reason FeCl_3 was mixed with CuCl_2 into one catholyte. This catholyte was tested in single cells #1196 thru #1225. These cells are divided in three groups by using three different anodes - 20 % LiAl, 28 % LiAl, and anode #7. Two catholytes were prepared. One catholyte contained 50 % FeCl_3 and 50 % CuCl_2 and one catholyte contained 50 % FeCl_3 and 50 % CuCl_2 . The results of these tests are presented in Table 22.

TABLE 22 $\text{FeCl}_3/\text{CuCl}_2$ SINGLE CELL TEST DATA

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀		NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohms	Tests at 200°C
1197	1.64	328	55	92	10.2	13.7	.81	50 ^m /o $\text{FeCl}_3/\text{CuCl}_2$ 28 ^w /o LiAl
1196	2.31	42.3	118	195	11.7	17.6	5	
1198	2.34	17.0	485	970	11.6	19.6	12.6	
1200	1.55	175	100	155	16.3	22.5	.81	50 ^m /o $\text{FeCl}_3/\text{CuCl}_2$ 20 ^w /o LiAl
1199	2.19	40.1	230	450	12.3	20.3	5	
1201	2.34	17.0	504	1122	12.3	22.5	12.6	
1203	1.28	145	72	109	7.99	8.26	.81	50 ^m /o $\text{FeCl}_3/\text{CuCl}_2$ Anode #7
1202	2.18	39.9	234	544	12.6	23.8	5	
1204	2.24	16.3	557	947	12.3	18.2	12.6	
1206	1.56	176	75	105	12.9	16.3	.81	50 ^w /o $\text{FeCl}_3/\text{CuCl}_2$ 28 ^w /o LiAl
1205	2.20	40.3	240	490	13.1	22.3	5	
1207	2.38	17.3	527	1292	13.1	26.2	12.6	
1209	1.64	185	80	106	14.7	18.0	.81	50 ^w /o $\text{FeCl}_3/\text{CuCl}_2$ 20 ^w /o LiAl
1210	2.26	41.4	224	631	13.0	28.8	5	
1208	2.39	17.4	525	887	13.1	19.4	12.6	
1212	1.56	176	80	131	13.2	19.0	.81	50 ^w /o $\text{FeCl}_3/\text{CuCl}_2$ Anode #7
1211	2.19	40.1	242	547	13.1	24.2	5	
1213	2.24	16.3	586	911	12.3	17.2	12.6	

Figure 15 is a sketch of a typical FeCl_3 discharge curve, a typical CuCl_2 curve, and a typical $\text{FeCl}_3/\text{CuCl}_2$ curve. The effect of mixing the FeCl_3 was to increase the peak voltage but the lifetimes became shorter. Due to the relatively large increment between the peak voltages of CuCl_2 and FeCl_3 , the main effect of mixing the two in one catholyte was to create a high voltage plateau which lowered the energy density in a manner similar to the lowering

of the energy density due to the MoCl_5 spike. That is, mixing two cathode species does not appear to be feasible unless the peak voltages are close together. The cell did not appear to begin to utilize the CuCl_2 until the 80% of peak had already been reached.

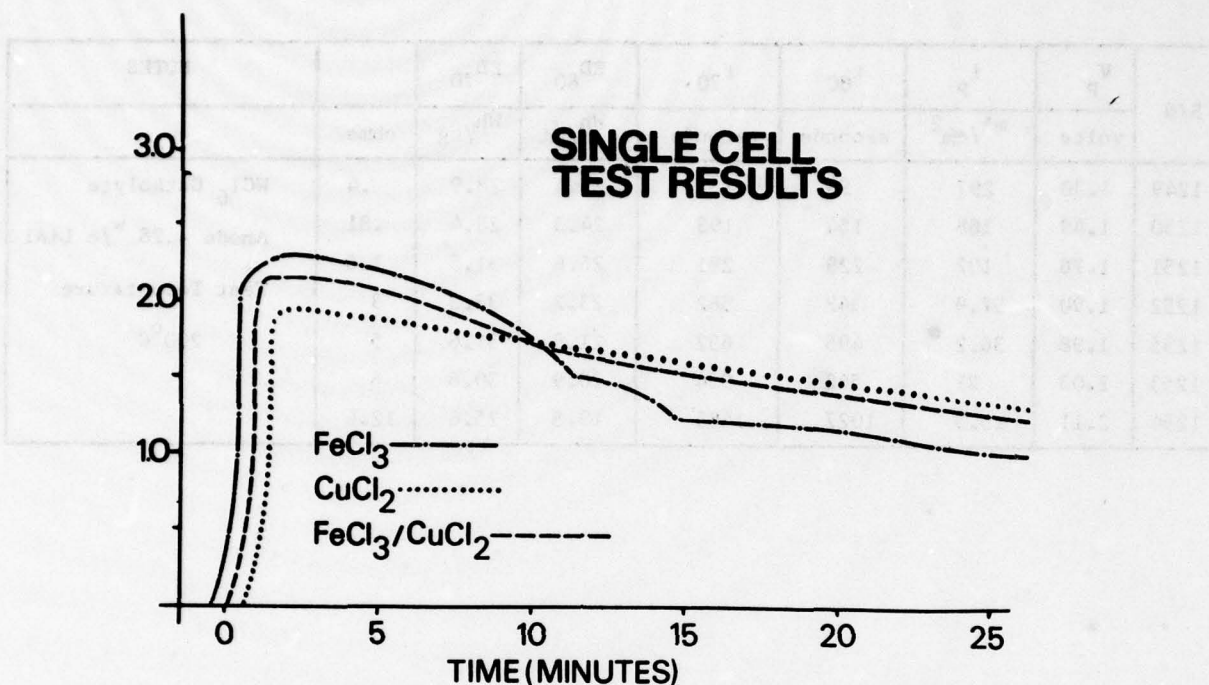


Figure 15. Typical Discharge Curves for FeCl_3 , CuCl_2 and $\text{FeCl}_3/\text{CuCl}_2$ type Cells

Another cathode chloride was tungsten hexachloride, WCl_6 . WCl_6 catholyte was tested by single cell with both a 20^{w/o} LiAl anode and a 28^{w/o} LiAl anode. One cell was tested with a catholyte which contained both CuCl_2 and WCl_6 . Table 23 is the single cell test data collected at 200°C with an anode of 28^{w/o} LiAl. Table 24 is the single cell test data for the cells at constant 5 ohm load and various temperatures.

TABLE 23 SINGLE CELL TEST DATA FOR WCl_6 CATHOLYTE

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀		NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohms	
1249	1.30	297	98	132	23.4	28.9	.4	WCl_6 Catholyte Anode - 28 ^{w/o} LiAl Test Temperature 200°C
1250	1.49	168	154	193	24.3	28.4	.81	
1251	1.76	107	229	291	26.6	31.5	1.5	
1252	1.90	57.9	342	562	23.2	33.3	3	
1255	1.98	36.2	495	632	21.5	31.6	5	
1253	2.03	31	562	934	20.9	30.6	6	
1254	2.11	15.3	1027	1485	19.5	25.6	12.6	

TABLE 24 SINGLE CELL TEST DATA FOR WCl_6 CATHOLYTE

S/N	V_p	i_p	t_{80}	t_{70}	ED ₈₀	ED ₇₀	T	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	°C	
1247	1.84	33.7	276	536	9.91	18.7	160	WCl_6 Catholyte Anode - 28 ^{w/o} LiAl Load Resistance 5 ohms
1248	1.95	35.7	500	878	21.2	32.2	180	
1255	1.98	36.2	495	832	21.5	31.6	200	
1256	2.03	37.1	424	776	19	30.1	220	
1257	2.04	37.3	288	362	13.5	15.8	240	
1258	2.04	37.3	226	285	10.7	12.6	260	
1259	2.12	38.8	130	169	6.74	8.07	280	

Figure 16 illustrates data from Table 23. The dotted curves represent MoCl_5 data generated previously. It can be seen that WCl_6 is at least as good as MoCl_5 at high current densities and is better than MoCl_5 at low current densities.

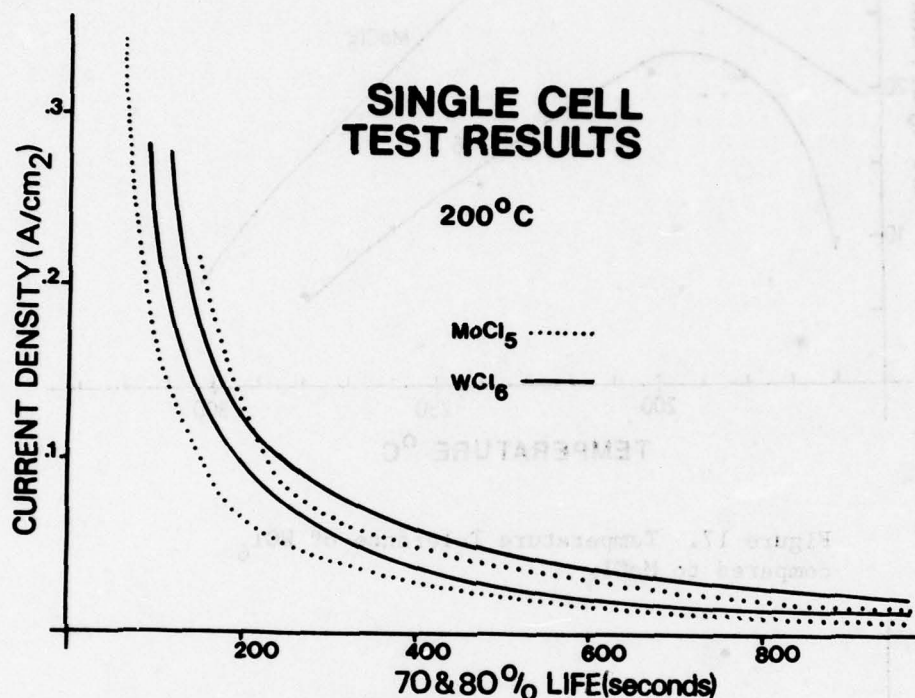


Figure 16. WCl_6 Single Cell Test Results compared to MoCl_5 Test Results

Figure 17 illustrates data from Table 24. It can be seen that WCl_6 does not have quite as wide a temperature tolerance range as MoCl_5 has.

Figure 18 shows a typical WCl_6 cell discharge curve relative to a typical MoCl_5 cell discharge curve. There is a tendency to produce a spike with WCl_6 but not as severely as with MoCl_5 . This reduced tendency for WCl_6 explains why WCl_6 performance looks so good compared to MoCl_5 .

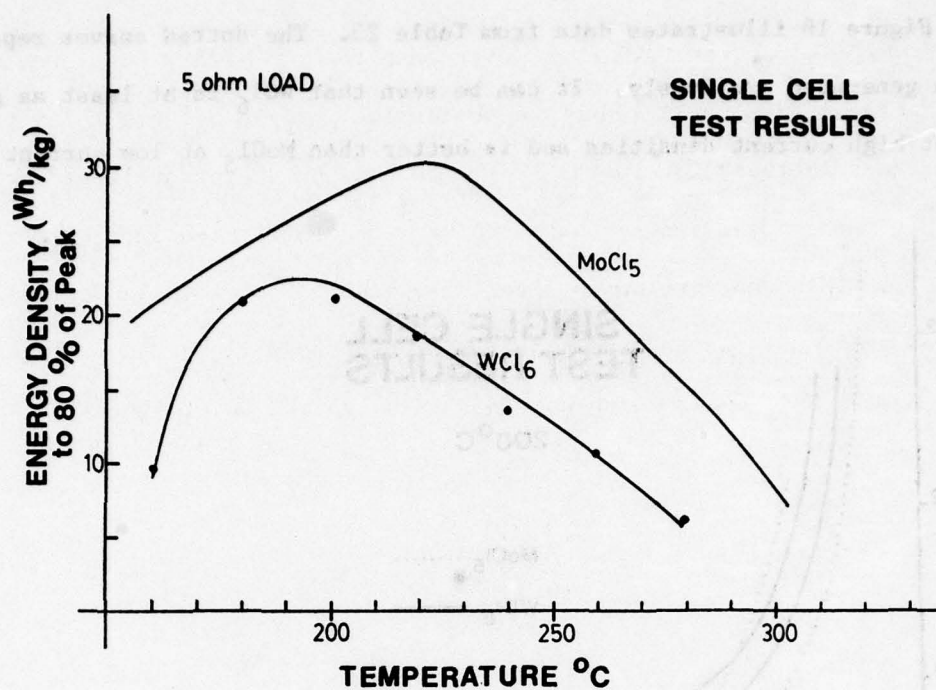


Figure 17. Temperature Tolerance of WCl₆ compared to MoCl₅

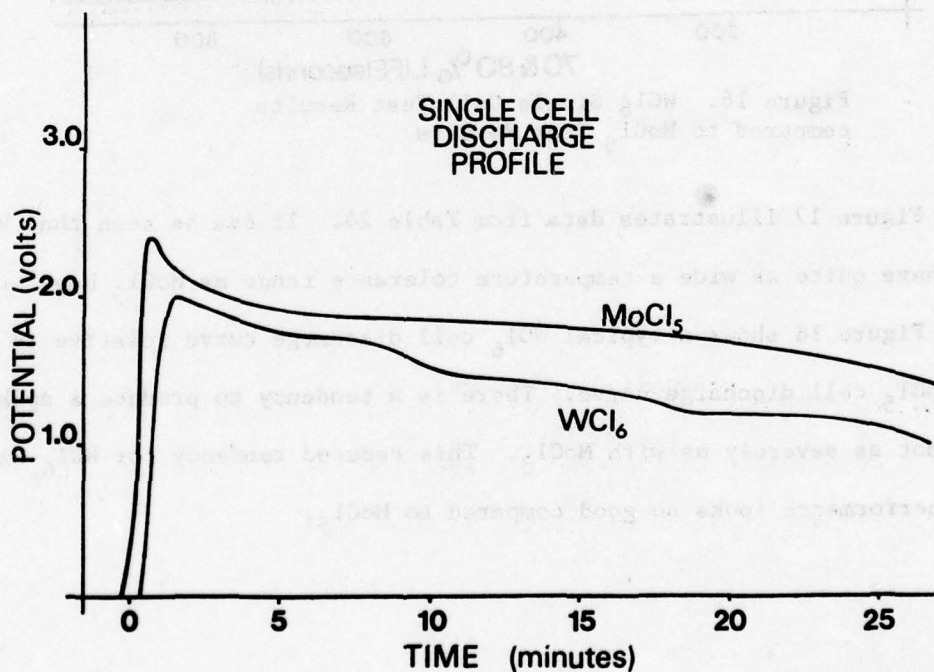


Figure 18. A Typical WCl₆ Discharge Curve

WCl_6 has a peak voltage even lower than FeCl_3 . It has been previously mentioned that FeCl_3 and CuCl_2 cannot be successfully mixed because their peak voltages are so relatively far apart. WCl_6 and CuCl_2 have peak voltages which are relatively much closer and so there may be some benefit realized by mixing WCl_6 and CuCl_2 . This was done and one cell has been tested (Single Cell #1260). This cell was about as good as a WCl_6 cell. More tests will be made. Figure 19 displays a typical $\text{WCl}_6/\text{CuCl}_2$ curve compared to a typical CuCl_2 discharge curve.

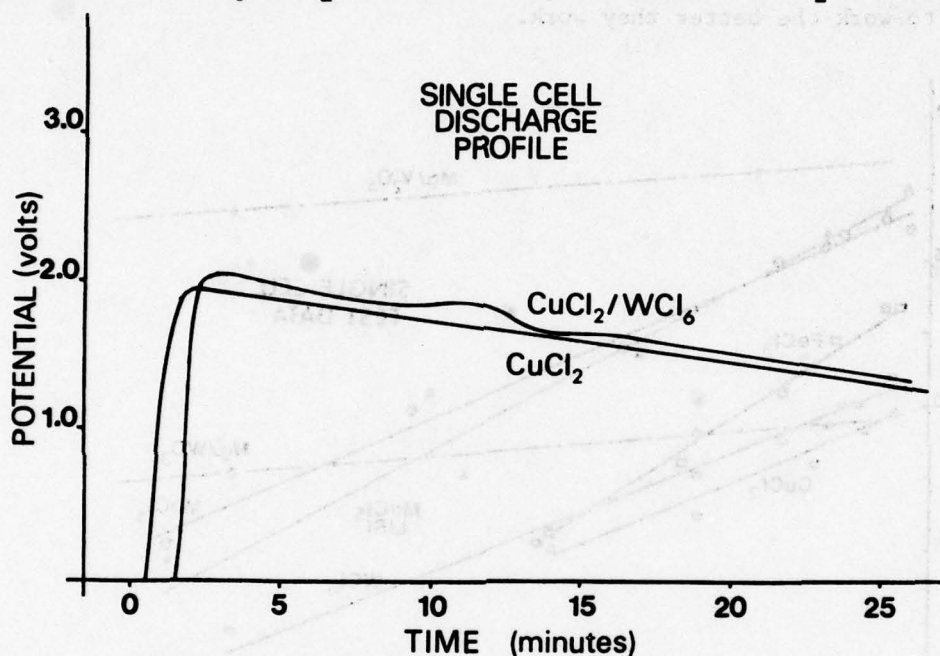


Figure 19. A Typical $\text{CuCl}_2/\text{WCl}_6$ Discharge Curve

To summarize, WCl_6 initially appears to be a good cathode material with a relatively low peak voltage and a poor temperature tolerance. One possible use of WCl_6 is as an additive to increase the early voltage for the CuCl_2 catholytes. WCl_6 is presently an expensive material.

An interesting trend has been noted while testing these various cathode materials. It was first noted that cells made with MoCl_5 reached a maximum energy density as the current density increased. That is, the harder the cells worked the better they worked. Other cathode materials did not function this way. FeCl_3 cells displayed no correlation between energy density and current density. CuCl_2 cells behaved just opposite to MoCl_5 cells. That is, as the current density decreased the energy density increased, or, the easier the cells are allowed to work the better they work.

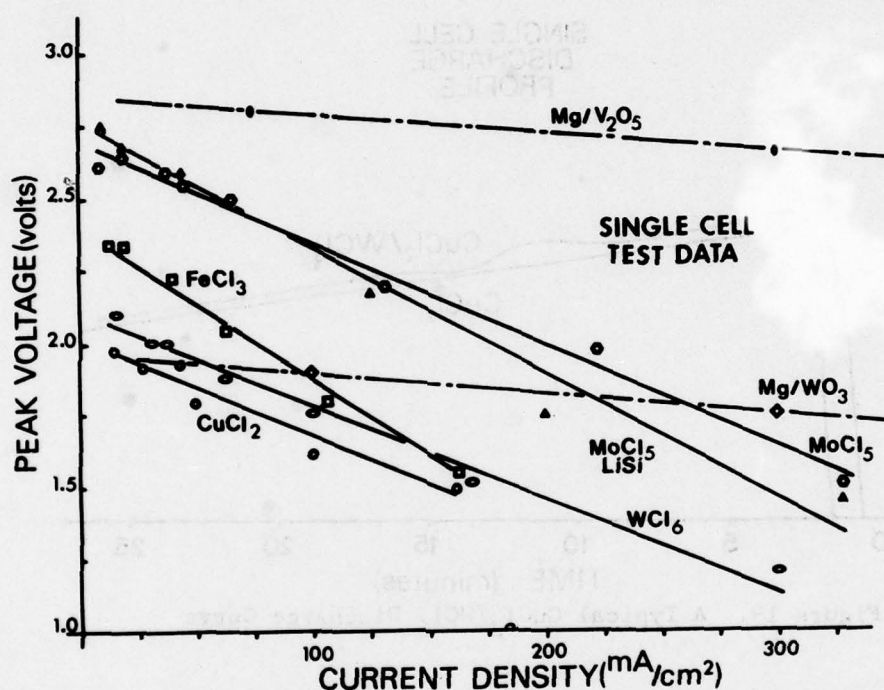


Figure 20. Polarization Curves for the NaAlCl_4 System compared to the KCl-LiCl System

Figure 20 illustrates how the peak voltages vary with current density for a number of cathode and anode systems tested for this project. The behavior of MoCl_5 , CuCl_2 , FeCl_3 , and WCl_6 vs. a LiAl anode is plotted. In addition to this MoCl_5 is plotted vs. a LiSi anode. The dashed lines represent the behavior of the Eureka production systems $\text{Mg/V}_2\text{O}_5$ and Mg/WO_3 . It appears that the slopes of all of the lines generated for NaAlCl_4 cells are similar and the slopes for all the KCl-LiCl lines are also similar. Furthermore, the slope of the KCl-LiCl lines is much closer to zero than the NaAlCl_4 lines. This indicates a severe polarization which may be a characteristic of the NaAlCl_4 system but which is not present in the KCl-LiCl system.

It is now known whether this polarization or any other polarizations which may be taking place in the cell are located at the anode or the cathode. It is proposed to study these polarizations with the use of a reference electrode inserted in the anolyte layer. This should indicate the relative sizes of the polarizations at both the anode and cathode.

It has been decided to try an aluminum reference electrode. This will consist of an aluminum wire inserted in a glass capillary filled with anolyte and stopped with a plug (a salt bridge) of a mixture of 75 w/o NaAlCl_4 and 25 w/o Cab-O-Sil.

In summary, four cathode chlorides have been used to make cells. MoCl_5 can be considered the regular cathode material and FeCl_3 , CuCl_2 and WCl_6 are alternate cathode chlorides. Testing displays unique discharge characteristics.

FeCl_3 was the first material tested. The peak voltage of FeCl_3 is almost as good as MoCl_5 with the advantage of no high voltage activation spike. FeCl_3 has the disadvantages of not being able to carry a high current, a shorter lifetime due to poor voltage regulation, a poor temperature range, and a moisture sensitivity at least as poor as MoCl_5 .

CuCl_2 has one large disadvantage: a relatively low peak voltage. However, CuCl_2 has some large advantages: a flat discharge curve for longer life, a wide range of temperature tolerance, much less sensitivity to moisture and CuCl_2 can carry a respectable current.

WCl_6 is a good cathode chloride but it is expensive, has a tendency to form a spike and has poor voltage regulation.

The best material for a high energy density battery is still MoCl_5 . However, for a long life battery CuCl_2 is the best material because of the relative flatness of the discharge curve.

SECTION X

ALTERNATE CATHODE MATERIALS (NOT CHLORIDES)

The first alternate cathode material was not a chloride but a pyrite, FeS_2 . Tests indicate that this material would only be good for a high temperature battery.

A test catholyte was prepared using FeS_2 instead of MoCl_5 . The DSC spectrum of this material displayed a large exotherm at 167°C . One would normally expect to find a large endotherm at that temperature which would be interpreted as the heat of fusion. It appeared that the FeS_2 was reacting with the electrolyte.

This first catholyte was diluted with 50 ^w/o anolyte. When the diluted catholyte was tested an exotherm did not appear but there was a small endotherm at 143°C and a large endotherm at 167°C. This is actually very similar to the DSC spectrum usually obtained for a somewhat moist anolyte.

A third catholyte was prepared by mixing 66 ^w/o FeS₂ with 34 ^w/o anolyte. This material produced a DSC spectrum similar to a moist anolyte with no evidence of an exotherm.

A second sample of the first catholyte was tested and again the large exotherm was noted. This sample was cooled and tested again. On the second heating the only thermal feature noted was an endotherm at 170°C. The exotherm had not appeared upon reheating the sample.

There was no explanation for the inconsistent appearance of an exotherm near the melting points of these materials. Perhaps the heat of reaction for FeS₂ and the anolyte is very close to the heat of melting and the exotherm (or endotherm) can be lost in samples of different relative FeS₂ concentrations. To test this a series of Anolyte/FeS₂ mixtures was prepared and DSC spectra for these generated.

A series of mixtures of anolyte and FeS₂ were made and DSC spectra were generated for each. The sample program was:

- | | |
|-------------------------|--------------------------|
| 1) pure anolyte | 5) 66% FeS ₂ |
| 2) 15% FeS ₂ | 6) 90% FeS ₂ |
| 3) 30% FeS ₂ | 7) 100% FeS ₂ |
| 4) 50% FeS ₂ | |

Each sample was heated, cooled, and reheated.

As the sample became more concentrated with FeS₂ the DSC spectra became more exothermic. The spectra did not consist of a number of well defined features which changed progressively as the percentage of FeS₂ increased.

A catholyte was made of 45 ^{w/o} A #1030 with 45 ^{w/o} FeS₂ and 10 ^{w/o} graphite. This material was made into cells with Anolyte #1030 and 20 ^{w/o} LiAl anode. These were used for single cell test #1152 to #1158. Table 25 is a tabulation of the test results.

TABLE 25 TABULATION OF FeS₂ SINGLE CELL TEST RESULTS

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	LOAD	NOTES
	volts	mA	seconds	seconds	wh/kg	wh/kg	°C	ohms	-
1152	1.36	24.9	35	46	.719	-	200	5	C#1039, A#1030, 20 ^{w/o} LiAl
1153	1.59	11.5	77	137	.857	-	200	12.6	C#1039, A#1030, 20 ^{w/o} LiAl
1154	1.21	22.1	91	291	1.38	3.61	250	5	C#1039, A#1030, 20 ^{w/o} LiAl
1155	1.55	28.3	26	177	0.68	-	300	5	C#1039, A#1030, 20 ^{w/o} LiAl
1156	1.49	27.3	160	175	3.56	-	340	5	C#1039, A#1030, 20 ^{w/o} LiAl
1157	1.46	26.7	74	134	1.92	2.89	380	5	C#1039, A#1030, 20 ^{w/o} LiAl
1158	1.43	26.2	99	207	2.41	4.09	420	5	C#1039, A#1030, 20 ^{w/o} LiAl

The conclusions of all cell testing are:

- a) The FeS₂ cathode is far inferior to any cathode chloride tested so far,
- b) The FeS₂ performs better at higher temperatures.

In conclusion it can be stated that FeS₂ does not appear to be a good cathode material and further use of this material is not anticipated with this electrolyte.

SECTION XI

BINDER ADDED TO CATHOLYTE

Post mortem examinations of many of the first MoCl_5 batteries showed symptoms of possible electrolyte flow. To correct this possible problem a catholyte was prepared which contained 10 % Cab-O-Sil.

An anolyte was prepared by mixing and fusing 40 % Cab-O-Sil into NaAlCl_4 . This anolyte was then mixed into a test catholyte.

26 mg 40 % Anolyte

56 mg MoCl_5

18 gm Graphite

The test catholyte then contained 10 % Cab-O-Sil.

The DSC spectrum of the catholyte displayed very small peaks. The tests were repeated with a larger sample but once again only very small peaks were observed.

It was difficult to make cells with this material because the bulk density of the catholyte was so low. One cell was finally constructed and it had a total weight of only 2.8 grams instead of 4.1 grams. The lifetime of this cell was very poor.

Adding binder to the catholyte will only be practical when some other method of mixing is available (for example, freon blending).

SECTION XII

BINDERS (NOT CAB-O-SIL) IN THE CATHOLYTE

Some of the earliest work done with this battery system indicated that some binder might be needed in the catholyte. This was unsuccessfully tried by fusing Cab-O-Sil into an anolyte and mixing this into the catholyte. The resulting catholyte was not dense enough to be practical.

However, in some more recent work it became advantageous to make some anolytes by mechanically mixing kaolin with NaAlCl_4 instead of the usual fusion of Cab-O-Sil into NaAlCl_4 . In order to prevent flow of the molten salts it was necessary to use 40 % kaolin. Catholytes made with this anolyte contained 10 % kaolin. These cells were just as dense as regular test catholyte and there was no difficulty making cells.

The cells tests were rather unexciting. The peak voltages and energy densities were slightly lower than for cells made with regular test catholyte. This was because of a significant increase of resistance in the cells. There was no evidence of flow in any of these cells. Kaolin can be used as a binder in situations where fusing the electrolyte is not desirable.

SECTION XIII

FREON BLENDING

The process of freon blending of anolyte and catholyte materials is being considered. All necessary materials and equipment have been ordered and

received. However, care is being taken to prevent freon vapors from entering the open flames associated with the dry room air driers. A special fume hood has been designed for installation in a dry room, which will exhaust outside the building.

SECTION XIV

ALTERNATE ANODE ALLOYS

Early work with this battery system demonstrated the presence of a high voltage activation spike. It was felt that the size and shape of this spike was in some way dependent upon the activity of the lithium in the lithium anode. Mostly in an effort to test this theory a number of alternate anodes have been made and tested.

The several anodes which were tested shall now be listed.

Anode #1 = 28 ^{w/o} LiAl alloy

Anode #2 = 20 ^{w/o} LiAl alloy

Anode #3 = 1/3 Al with 2/3 LiAl alloy (20 ^{w/o})

Anode #4 = 2/3 Al with 1/3 LiAl alloy (20 ^{w/o})

Anode #5 = 1/2 Al with 1/2 LiAl alloy (28 ^{w/o})

Anode #6 = 26.6% Al

53.4% LiAl (20 ^{w/o})

20.0% A #1030

Anode #7 = 2/5 Al & 2/5 LiAl (20 % w/o) & 1/5 A #1030

Anode #8 = LiSi alloy which contains 58 % w/o Lithium

Anode #9 = 50 % w/o Al and 50 % w/o LiSi alloy

Anode #10 = 25 % w/o Al and 75 % w/o LiSi alloy

Anode #11 = 40 % w/o LiAl alloy

Single cell results with anode #1 & #2 have been previously described. There is very little difference between 28 % w/o and 20 % w/o LiAl except for a slight reduction in the height of the high voltage activation spike. This reduction is too small to be a "cure" for the spike problem and is usually perceived as a lower peak voltage. Therefore, it was concluded in previous work that 28 % w/o LiAl was a superior anode material. However, consciousness of the spike makes this not necessarily true.

It was felt that the small change in the size and shape of the spike was caused by a reduction in Li in the anode so an anode was prepared by mixing 33.3 gm of Al granules with 66.7 gm 20 % w/o LiAl. The Al was sieved and only the material which passed thru a #40 sieve was used. This was done because of the difficulty in obtaining LiAl alloys which contain less than 20 % w/o Li, in a useful form. This was named anode #3.

Anode #3 was used with A #1030 and a test catholyte RC-13 to make test cells. These cells were tested and numbered 1114 thru 1119. These data are tabulated in Table 26.

It can be seen from these data that the peak voltage is still quite good. Observing the discharge curves it shows that the spike is almost entirely gone. However, the curve still dropped off too quickly resembling the shape of a negative exponential curve.

TABLE 26 SINGLE CELL TEST RESULTS
FOR CELLS USING ANODE #3

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	LOAD	NOTES
	volts	mA	seconds	seconds	wh/kg	wh/kg	°C	ohms	
1114	2.49	45.6	400	604	25.6	40.0	200	5	1/3 Al & 2/3 LiAl (20 ^{w/o})
1115	2.58	18.7	792	1232	21.7	30.6	200	12.6	
1116	2.02	228	130	163	38.1	-	200	.81	
1117	2.43	44.5	486	691	30.0	-	180	5	
1118	2.41	44.1	488	716	29.5	-	160	5	
1119	2.45	44.8	91	239	6.28	-	300	5	

In a further attempt to smooth out the discharge curve another anode was mixed with 2/3 Al & 1/3 LiAl (20^{w/o}). This anode was tested in cells #1120 thru 1135. There was no significant change except that the 70% life became shorter. It appeared that the anode was running out of lithium too quickly. Therefore another anode was made of 1/2 Al & 1/2 LiAl (28^{w/o}). This anode produced a little smaller energy density with no significant change in the shape of the discharge curve.

Two more anodes were made which contained anolyte. That is, 20^{w/o} anolyte was mixed into the anode material. This was done to, both, increase the conductivity of the anode and to act as a thermal buffer for the anode. This was done to anode #3 (the mixture was renamed anode #6) and to a mixture of 1/2 Al & 1/2 LiAl (20^{w/o}) (named anode #7). The materials were tested in cells #1136 thru #1151. There was no significant improvement with these salt containing anodes except than the activation time was shorter.

To summarize, adding Al powder to the LiAl alloys had the effect of minimizing the spike and flattening the discharge curve. The discharge curve was in general shaped like a negative exponential curve with the 80% life about 2.5 times larger than the 90% life and the 70% life about 7 times longer than the 90% life. As the concentration of lithium in the anode became less so did the 70% life although the 90% and 80% lives were not particularly affected. Adding 20 ^{w/o} anolyte to the anode increased the energy density about 5%. Adding Al to the anode tended to slow activation but adding anolyte restored the activation. The 90% life was improved most with less significant improvements in the 80 and 70% lifetimes.

The LiSi alloy was first tested in single cell tests #1226 to #1244. These included some cells with MoCl₅ catholyte and CuCl₂ catholyte. This also includes one anode mixed with 50 ^{w/o} Al powder.

Table 27 is a tabulation of all the single cells made with MoCl₅ catholyte and tested at 200°C with varying loads.

TABLE 27 SINGLE CELL TEST DATA

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm	
1229	1.40	334	129	160	39.8	46.1	.4	MoCl ₅ /LiSi 200°C
1227	1.76	199	180	226	39.9	46.6	.81	
1232	2.21	135	171	233	31.3	39.0	1.5	
1233	2.30	70.1	370	-	35.5	-	3	
1226	2.48	45.4	474	694	31.3	41.6	5	
1228	2.64	19.2	810	1240	23.6	32.7	12.6	
1234	2.75	10.1	960	1810	11.3	21.6	25	

These data are illustrated with Figure 21. It can be seen from Figure 21 that the LiSi appears to make a significant improvement in the lifetime at high current densities. There was little improvement at low current densities. This has exaggerated the "the harder you work it the better it works" trend for MoCl_5 catholytes. Just the opposite is true for CuCl_2 . This has been previously noted for CuCl_2 with an LiAl anode. The WCl_6 seems to behave similarly to MoCl_5 .

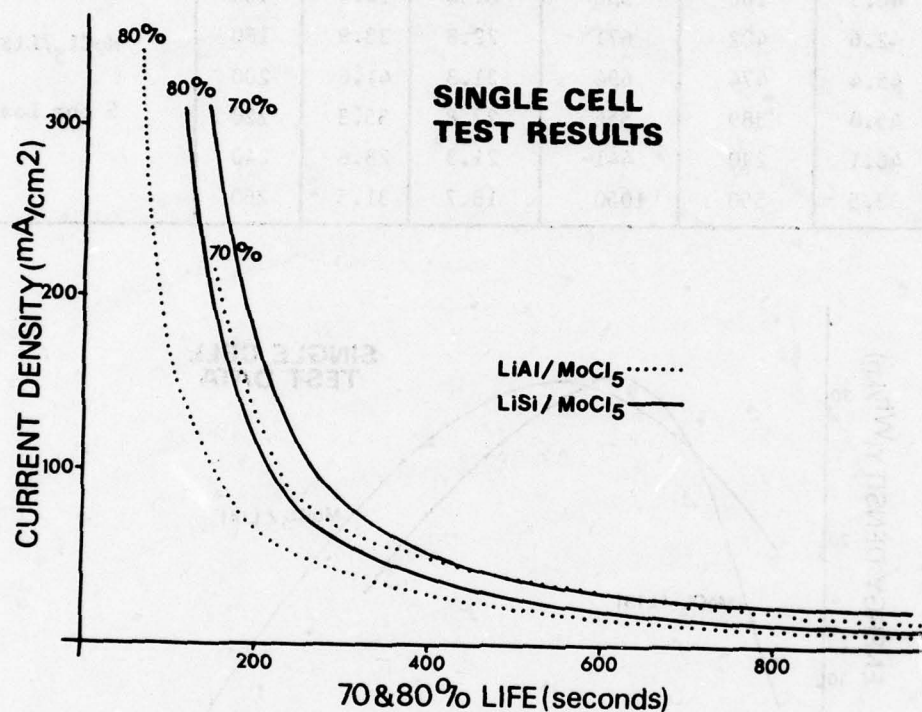


Figure 21. A Comparison of LiAl and LiSi Single Cell Test Results

Table 28 is a tabulation of the single cell test data for $\text{MoCl}_5/\text{LiSi}$ cells made at constant 5 ohm load and various temperatures.

The data in Table 28 are illustrated in Figure 22. The use of LiSi did not affect the temperature tolerance range of MoCl_5 catholytes much at all.

TABLE 28 SINGLE CELL TEST DATA

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	°C	
1230	2.20	40.3	166	336	8.54	14.8	160	MoCl ₅ /LiSi 5 ohm Load
1231	2.33	42.6	402	671	22.8	33.9	180	
1226	2.48	45.4	474	694	31.3	41.6	200	
1236	2.46	45.0	389	556	27.8	35.3	220	
1237	2.52	46.1	290	441	21.3	28.6	240	
1238	1.83	33.5	550	1050	18.7	31.5	260	

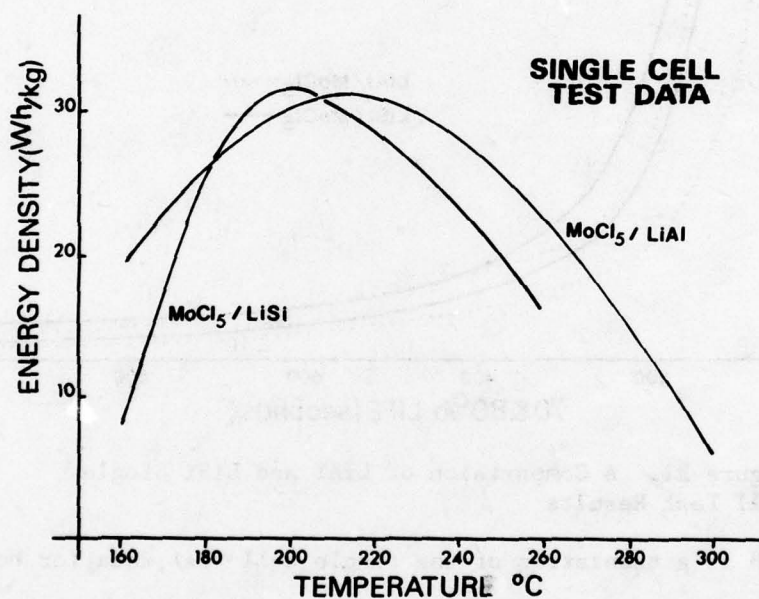


Figure 22. The Temperature Tolerance of LiSi Cells

Using LiSi with MoCl_5 catholyte did greatly lessen the effect of the activation spike. This significantly changes the shape of a typical discharge curve for a MoCl_5 catholyte as can be seen in Figure 23. This is interesting because using LiSi alloy with CuCl_2 caused a spike to form. Because of this, granular aluminum was mixed with the LiSi to make Anode #9. Mixing Al with LiAl alloy reduced the spike with MoCl_5 catholyte and adding Al to the LiSi reduced the spike with the CuCl_2 catholytes.

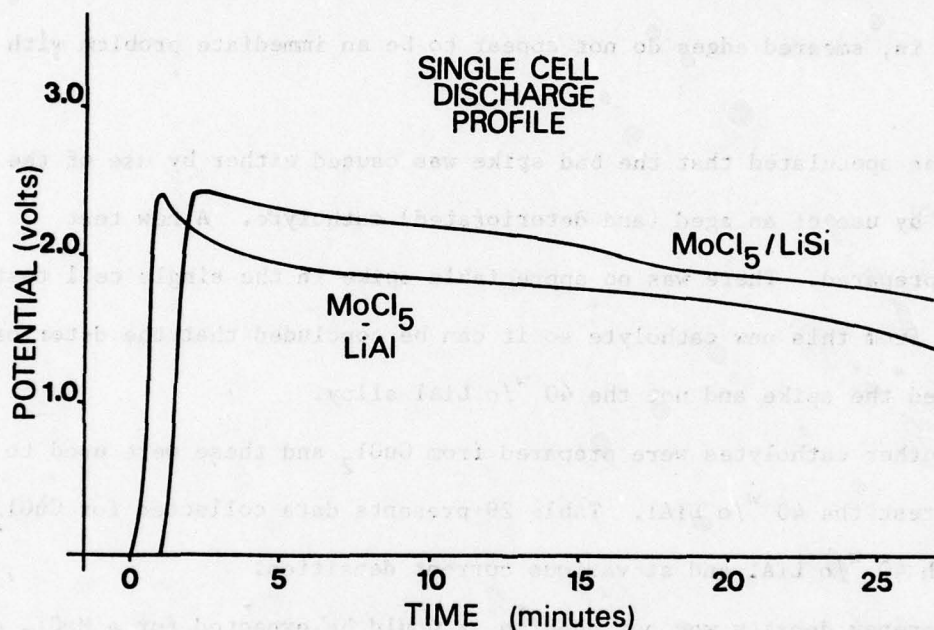


Figure 23. The Effect of LiSi upon a Typical MoCl_5 Discharge Curve

To summarize, LiSi alloy was tested with MoCl_5 and produced a slightly superior cell. The LiSi caused a spike to form with the CuCl_2 system. LiSi produced a cell with a very high energy density.

Some 40 ^w/o lithium LiAl alloy was tested. The first tests were run with single cells made with a catholyte that had been stored about two months in a screw cap jar in a dry room. These cells displayed a severe spike. The spike was so bad that the cells were not treated quantitatively.

It was noticed while preparing these bad cells that the edges appeared to smear more than usual. For this reason some cells had their edges abraded with emery paper. However, this treatment made no noticeable effect on the cell performance. This has also been the case for other cells filed earlier in this project. That is, smeared edges do not appear to be an immediate problem with this system.

It was speculated that the bad spike was caused either by use of the 40 ^w/o LiAl or by use of an aged (and deteriorated) catholyte. A new test catholyte was prepared. There was no appreciable spike in the single cell tests for cells made from this new catholyte so it can be concluded that the deteriorated catholyte caused the spike and not the 40 ^w/o LiAl alloy.

Two other catholytes were prepared from CuCl_2 and these were used to make cells to test the 40 ^w/o LiAl. Table 29 presents data collected for CuCl_2 cells made with 40 ^w/o LiAl and at various current densities.

The energy density was not as high as would be expected for a MoCl_5 cell in the moderate to high current density regions. The energy density was quite good for the low current density discharges. This has been noted before in previous progress reports. Cells #1275 & #1278 had "record" high energy densities. Once again the CuCl_2 appears to be best for a long life low current density battery.

Table 30 and Figure 11 illustrate the superior temperature tolerance of CuCl_2 .

TABLE 29 40 ^w/o LiAl SINGLE CELL TEST RESULTS

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	ohm	
(1272) (1279)	1.60	180	71	116	12.4	17.7	.81	CuCl ₂ Catholyte 40 ^w /o LiAl Anode 200°C
1277	1.73	106	152	268	16.5	25.3	1.5	
1276	1.82	55.5	372	650	22.1	33.8	3	
(1270) (1271)	1.87	34.2	628	1263	23.2	40.1	5	
(1273) (1275)	1.92	13.9	2695	4150	41.2	57.4	12.6	
1278	2.05	7.5	5256	7816	43.8	60.2	25	

TABLE 30 40 ^w/o LiAl SINGLE CELL TEST RESULTS

S/N	V _p	i _p	t ₈₀	t ₇₀	ED ₈₀	ED ₇₀	T	NOTES
	volts	mA/cm ²	seconds	seconds	Wh/kg	Wh/kg	°C	
1280	1.89	34.8	763	1233	28.7	41.4	180	5 ohm Load CuCl ₂ Catholyte 40 ^w /o LiAl Anode
1281	1.88	34.4	665	1100	25.6	37.3	240	
1282	1.89	34.6	595	835	23.4	29.9	280	
1283	1.88	34.4	245	1170	9.36	34.8	300	
1284	1.93	35.3	435	1295	17.2	41.5	320	
1285	1.95	36.7	346	982	14.0	32.5	340	

To summarize, the 40 ^w/o LiAl makes an excellent anode material. With the MoCl₅ catholyte the tendency to form a spike is enhanced. The voltage and energy density are enlarged for both the CuCl₂ and the MoCl₅ system. The combination of 40 ^w/o LiAl anode, CuCl₂ catholyte and low current density produced excellent cell performance.

SECTION XV

CELL REPRODUCIBILITY

A cell which has good reproducibility can be fabricated repeatedly over a relatively long period of time, maintaining consistent physical properties (weight, thickness, shape, etc.), and resulting in a finished cell which functions in a repeatable and predictable manner.

In the early days of this program reproducibility was very poor due to the presence of the activation spike and due to the poor cell fabrication methods. However, fabrication methods have been improved and the spike is better understood than before.

The test cells are now made on a manually operated hydraulic press fitted with a 1.469" diameter circular die. It has proven very easy to make three layer thermal cells on this press. The total cell weight can be easily maintained at 4.10 grams \pm 0.1 gram. The cells produced are rigid, firm with only very slight bowing, and with only a slight tendency to crack or delaminate. The cell edges do not appear to smear appreciably.

By controlling the spike the cell performance can be quite reproducible. For example, examine once again the data of pages 26 & 27. These cells were made at different times, months apart, from different materials, for different purposes and still performed quite similarly.

This was not the case with all of the cells produced. The cell made with FeS_2 in the catholyte bowed, cracked, and started to crumble within minutes after fabrication.

In conclusion, it can be stated that the cells for this program are quite reproducible and are at least as good as existing thermal cell systems.

SECTION XVI

CELL COMPATABILITY

Compatability refers generally, to the ability of the various battery components to exist together in one unit and specifically, to the degree of mutual degradation realized in any of these components. This is generally referred to as "storage life" for a reserve battery. The type of problems which appear are, viz., autoreduction of the cathode, autoxidation of the anode, volatile, corrosive gas forming due to a reaction of moist air with hygroscopic electrolyte material, etc.

Most of the compatability and storage problems found with this system center around the cathode chloride. The completed cells have a tendency to crack and crumble upon storage. Also, the anode layer turns dark on storage. In one instance some cells were stored in a screw cap jar in a dry room and slowly deteriorated over a one month period. Also, the cells and batteries have started displaying voltage before they are activated. This is called cold voltage.

All of these problems appear to be related to exposure to air. It is not known whether the active ingredient in air is O_2 , N_2 , H_2O vapor or what, but it appears that this system is much more subject to exposure problems than even conventional thermal battery systems.

There is also the possibility of self discharge. The cathode could be producing Cl_2 or HCl which is causing an autodischarge.

Regardless of what the causes are, these problems are going to need to be investigated before the storage life of the battery can be improved.

SECTION XVII

CELL PROCESSING AND FABRICATION

Two main problems have been incurred while making cells:

- 1) the cells tend to crumble, delaminate, and break before they can be used, and
- 2) it is difficult to shear the cells.

The breakage problem has already been mentioned as a storage problem.

Of more immediate interest are cells that break as they come out of the cell die. This problem can be cured by changing the ram pressure on the press. This pressure needs to be adjusted for almost every combination of anode, anolyte, and catholyte and can be easily determined by trial and error.

Sometimes the edges of a cell tend to smear and cause local shorting. This can usually be cured by making the cells oversize and punching out a smaller cell. However, these cells do not punch well. The LiAl anode is very brittle. It has been found that these cells can be punched with very sharp dies. The center hole has never been successfully punched in these cells but center holes can be drilled with common twist drills.

SECTION XVIII

BATTERY BUILDING AND TESTING

The first batteries of this contract have been made and tested. The first design was a 10 cell series stack in a 2 inch tall by 2 inch diameter steel

can. The design was the same as for batteries made for the feasibility study of this system except that the can was a different size and therefore there were some differences in insulation and in the header and match assembly. This design is extremely simple to reproduce and shall be considered a "test battery" until some major design change is made. Figure 24 is a diagram which represents the test battery design.

The cells were a disk, 1.469" diameter, with no center hole. The anode was $0.5 \pm .1$ gm 28 ^W/o LiAl alloy.

The anolyte was $1.3 \pm .1$ gm Anolyte #1004 and the catholyte was $2.3 \pm .1$ gm Catholyte #1015. The press compacting pressure was about 110,000 PSI. The total cell weight was 4.1 gm and the cell thickness was 0.070 inches.

The heat paper was LSS 15%, 430 cal/gm, 115 cal/in^2 , solid disk, 1.469" diameter. The cell connectros were 0.004" nickel. The fuze strips were LSS 8%, 430 cal/gm, 130 cal/in^2 , 5/16" wide.

The stack was pressed at 5,000 lbs. force and again pressed at 5,000 lbs. while in the case. The closing pressure was 300 lbs. of force on the header. The finished battery, S/N 1001, weighed 220 gms with a volume of 6.28 in^3 or 103 cm^3 .

The test was conducted at room temperature and the battery was discharged across a 35 ohm resistor. The activation was .81 seconds. The peak voltage was 22.3 volts (2.33 volts/cell), with a peak current of 637 mA and a peak current density of 58.3 mA/cm^2 . The energy density generated at 90% of peak was approximately 6.60 Wh/dm^3 . The internal resistance was measured once (at about 90% peak) and was 0.35 ohm (at about 90 seconds into life). The 90% life was 76 seconds, the 80% life was 150 seconds, the 70% life was 217 seconds, the 60% life

WRIGHT-PATTERSON TEST BATTERY

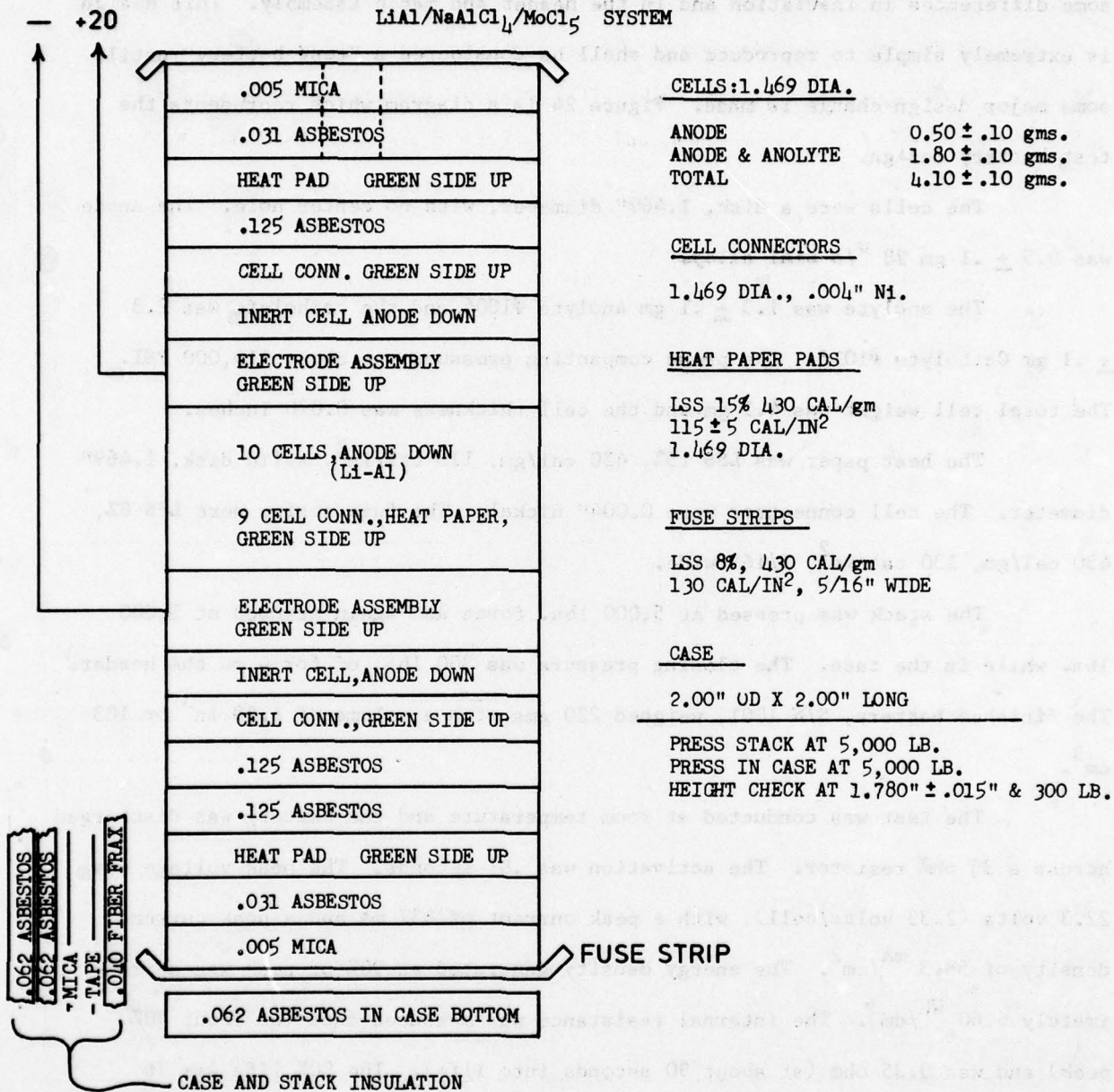


Figure 24. A Schematic Diagram of a Wright-Patterson Test Battery

was 403 seconds. The skin temperature was monitored with a thermocouple. The skin temperature was initially 27°C; 137°C after 242 seconds; 148°C after 400 seconds; 149°C after 455 seconds, and 150°C after 570 seconds. The peak temperature was 150°C. During this discharge there was no electrical noise. The battery did not vent or deform.

Battery #1002 was similar to #1001. This battery was fabricated with MoCl_5 cells, 115 cal/in² heat paper, 28 w/o LiAl anodes. This battery was the control unit for a series of batteries made for storage testing. Batteries #1002 to #1006 were all tested at room ambient temperature.

TABLE 31 STORAGE BATTERY TEST RESULTS

S/N	V _p	i _p	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	LOAD	NOTES
	volts	mA/cm ²	seconds	seconds	seconds	Wh/kg	Wh/kg	ohms	
1002	24.4	63.8	110	240	330	22.4	3.58	35	Control Unit
	+		+	+		+			
1003	22.8	59.6	30	134	326	10.3	1.96	35	Stored 28 days at 71°C before testing
	+		+	+		+			
1004	8.9	23	108	149	203	1.94	0.37	35	Stored 28 days at 71°C with + and - terminals shorted
	+		+	+		+			
1005	20.9	239	18	85	122	25.5	4.84	8	Stored 5 months at room ambient temperatures
	+		+	+		+			
1006	15.8	181	47	95	145	16.3	3.09	8	Stored 28 days at R.A. with + and - terminals shorted & 4 months at R.A. unshorted

Battery #1003 was similar to #1002 except that it was stored for 28 days in an oven maintained at 71°C. The battery was allowed to reach room temperature prior to testing. The battery produced a peak voltage and current of 22.4 volts and 651 mA with a current density of 59.6 mA/cm². The battery activated in 1.22 seconds. The lifetime to 90% of peak was 30 seconds; to 80% of peak was 134 seconds. The battery produced 10.2 Wh/kg based on 41 grams of cell weight and 1.96 Wh/kg based on 216 grams of total battery weight.

Comparing the results from Batteries #1002 and #1003 show that the hot storage definitely appeared to hurt the battery performance. The peak voltage was 6.5% lower, all of the early lifetimes were shorter and the energy density was 45% lower.

It was observed during single cell testing that short 90% and 80% lifetimes were indicative of a high voltage activation spike. Therefore, the relative failure of Battery #1003 could be caused by spike formation. However, the peak voltage was lower than before storage, not higher. While the hot storage may have caused a spike formation there is obviously material deterioration or the peak voltage would not have dropped off.

Battery #1004 was exactly like #1003 except it was stored with the plus and minus terminals shorted together. This battery had only about 1/3 as high a voltage (8.9 V_p) as the control battery. This battery only produced about 1/10 the energy density of the control unit. Obviously, the storage left the battery seriously depleted and deteriorated.

Battery #1005 was stored for about 5 months at 25°C before testing. The terminals were not shorted together. The peak voltage was smaller and the lifetimes shorter but the energy density to 80% was longer. This was because the test was 8 ohms instead of the usual 35 ohms. This allowed the maximum current density to

be up around 239 mA/cm^2 instead of 63 mA/cm^2 . The single cell studies indicate that the AllMo system produces a higher energy density at higher current densities. The lower voltage is also explainable with the heavier load. Therefore, the conclusion of this test seems to be that the battery was not seriously deteriorated by room temperature storage for 5 months.

Battery #1006 was the last battery of this series. It was stored at room temperature for the first month with the plus and minus terminals shorted together and with the short removed for the balance of the storage time. Battery #1006 performed only slightly worse than #1002.

Battery #1007 was made similar to Battery #1001 except that 96 cal/in^2 heat paper was used instead of 130 cal/in^2 . The activation was longer and the energy density was shorter so 115 cal/in^2 was decided upon as ideal.

Battery #1008 was made similar to #1002. Actually Battery #1008 was made prior to fabrication of #1002 and #1008 was used to prove in a new cell formula:

Anode $0.45 \pm .1 \text{ gm}$

Anode & Anolyte $2.20 \pm .1 \text{ gm}$

Cell $4.1 \pm .1 \text{ gm}$

The heat paper was 115 cal/in^2 . Since this battery performed well the storage batteries (later numbered #1002 thru #1006) were made similar to this.

Batteries #1009 & #1010 were made similar to #1002. These batteries were the first batteries tested after being conditioned for hot and cold testing. That is, each battery was placed in a chamber at either 60°C (#1009) or 55°C (#1010) for at least 4 hours prior to testing. The batteries were removed from the chamber and fired within 5 minutes to insure that the inside of the battery was truly at the test temperature during initiation.

AD-A068 889

EUREKA CO BLOOMINGTON IL EUREKA ADVANCE SCIENCE DIV
ADVANCED THERMAL BATTERIES.(U)
DEC 78 D M RYAN

F/G 10/3

UNCLASSIFIED

F33615-77-C-3147

AFAPL-TR-78-114

NL

2 OF 2
AD
A068889



END
DATE
FILMED

6--79
DDC

It can be seen from the data sheets that the batteries are quite well balanced (Table 32). The hot and cold batteries have almost the same output. The voltage is slightly lower for the cold battery and the internal resistance is higher. The activation is longer for the cold battery. These performance characteristics are normal for thermal battery operation. The energy densities were quite similar.

TABLE 32 HOT AND COLD BATTERY TEST RESULTS

S/N	Temp.	P _v	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	Spec. r at 90%	Spec. r at 80%
-	°C	volts	mA/cm ²	seconds	seconds	seconds	seconds	ohm·cm ²	ohm·cm ²
1009	60	23.1	264	1.13	22	72	103	2.36	3.21
1010	-55	21.4	245	1.70	22	75	119	528	6.41

Batteries #1011 & #1012 were made with cells that had 20 ^{w/o} LiAl anodes. #1011 was the cold test at -45°C and #1012 was the hot test at 85°C. These were excellent batteries with the highest energy densities yet measured at the 90% mark. The 20 ^{w/o} LiAl was used in an attempt to reduce the high voltage spike. There is no evidence of a spike on the cold test but the hot test did show a slight tendency to form a spike.

TABLE 33 HOT AND COLD TESTS FOR BATTERIES
MADE WITH 20 ^{w/o} LiAl ANODES

S/N	Temp.	P _v	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	Spec. r at 90%	ED ₈₀
-	°C	volts	mA/cm ²	seconds	seconds	seconds	seconds	ohm·cm ²	Wh/kg
1011	-45	20.2	231	2.27	52	95	118	7.21	4.08
1012	85	21.8	249	1.20	26	78	96	4.71	4.64

Batteries #1013 & #1014 were two more storage batteries. These batteries were constructed similar to #1002 except that the heat paper was 120 cal/in². These batteries were constructed 5 June 1978 and were tested 29 August 1978. They were stored at room temperature. Two batteries were made just to get an indication of repeatability.

There was an indication of spike formation (t_{90} 14 seconds and t_{80} at about 74 seconds) but the repeatability was quite good (see Table 34).

TABLE 34 STORAGE AND REPEATABILITY BATTERY TEST RESULTS.
THESE BATTERIES WERE TESTED AT ROOM TEMPERATURE ACROSS AN
8 OHM LOAD

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	ED ₉₀	ED ₈₀	Spec. r at 90%
-	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	ohm·cm ²
1013	21.8	249	1.80	14	74	108	0.97	4.59	11.2
1014	21.8	249	1.72	15	75	107	1.04	4.63	13.4

Batteries #1015 and #1016 were made to try the 40 % LiAl anode material. One battery was tested hot and one was tested cold (see Table 35).

TABLE 35 TEST RESULTS FOR BATTERIES MADE
WITH 40 % LiAl ANODES

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	Temp.	ED ₈₀	Spec. r at 90%
-	volts	mA/cm ²	seconds	seconds	seconds	seconds	°C	Wh/kg	ohm·cm ²
1015	23.2	265	1.03	16.3	60.7	97.3	85	3.63	4.30
1016	20.9	239	2.20	28.0	78.0	169	-45	3.78	7.75

The 40 % LiAl is not as dense as the 28 % or 20 % and so the anode became thicker. To compensate for this the anode weight was lowered from 0.45 gm to 0.40 gm and the total cell weight was lowered to 4.05 gm. There was a slight tendency to form a spike in both batteries. This is not as severe as expected from the single cell tests. Overall, these batteries did not perform as well as those with 20 % or 28 % LiAl anodes.

Batteries #1017 and #1018 were made to test the use of 58 % LiSi as an anode material. These batteries were also made with the 0.40 gm anode because of the less dense anode.

TABLE 36 TEST RESULTS FOR BATTERIES MADE
WITH 58 % LiSi ALLOY

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	Temp.	ED ₈₀	Spec. r at 90%
-	volts	mA/cm ²	seconds	seconds	seconds	seconds	°C	Wh/kg	ohm·cm ²
1017	24.0	274	0.95	21.3	61.1	86.2	85	3.90	4.08
1018	19.7	225	2.29	63.9	108	145	-45	4.63	8.16

There is a significant difference in these hot and cold tests. This also happened with Batteries #1015 & #1016. It appears that the 115 cal/in² heat paper may not be correct for these low density anodes. If this is the case, better thermal management should improve both types of battery. The cold LiSi battery produced the highest actual energy density at the 90% point of any battery yet tested. However, overall, this battery was not particularly any better than any of the others.

Batteries #1019 & #1020 were made to test the acidic CuCl₂ electrolytes.

TABLE 37 TEST RESULTS FOR BATTERIES MADE WITH ACIDIC
CuCl₂ ELECTROLYTES. THE TEST LOAD WAS 50 OHMS

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T _p	T _{Test}	Spec. r at 80%
-	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	°C	ohm.cm ²
1019	25.8	48.5	0.55	.78	1.2	117	.117	.022	155	75	X
1020	20.9	38.2	0.84	.30	220	530	9.42	1.79	99	-55	19.6

These batteries displayed a very severe "spike". This was unexpected because the CuCl₂ system had not displayed a spike during single cell testing. Experience shows that one of the factors that effects the spike is high temperature.

For this reason, a series of batteries were made with some thermal buffers in the cell connector assemblies. These thermal buffers were 0.005" thick pads of quinargo, inserted in the cell connector assembly between the heat paper and the nickel. Quinargo is an asbestos paper product manufactured by Johns-Manville.

Battery #1021 had quinargo placed in such a way as to protect the catholyte from thermal shock. Battery #1022 had a protected anode and battery #1023 had double quinargo protecting both electrodes. They were all tested across a 25 ohm load at room ambient temperature.

TABLE 38 TEST RESULTS FOR BATTERIES CONSTRUCTED WITH
QUINARGO HEAT BUFFERS IN THE CELL CONNECTORS

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T _p	T _{Test}	Spec. r at 80%
-	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	°C	ohm.cm ²
1021	20.2	73.9	1.11	99	169	284	15.5	2.93	219	25	18.0
1022	19.8	72.5	0.83	99	165	245	14.6	2.73	201	25	58.7
1023	20.7	75.9	1.0	77	129	207	12.4	2.33	240	25	30.0

The discharge curves were very straight. The thermal buffers appear to work as intended.

Three more batteries were made and tested. These batteries did not contain quinargo but they were made from cooler heat paper, 100 cal/in².

TABLE 39 BATTERY TEST RESULTS WITH A 25 OHM LOAD

S/N	V _p	i _p	Act.	t ₉₀	t ₈₀	t ₇₀	ED ₈₀ IDEAL	ED ₈₀ ACTUAL	T _p	T _{Test}	Spec. r at 80%
-	volts	mA/cm ²	seconds	seconds	seconds	seconds	Wh/kg	Wh/kg	°C	°C	ohm·cm ²
1024	21.7	79.4	0.54	1.06	113	325	10.4	1.98	141	75	4.71
	+				+		+		+		
1026	19.0	70.6	1.00	72	252	7350	19.7	3.74	117	25	15.1
	+				+		+		+		
1025	18.0	65.7	2.34	104	206	355	14.7	2.79	89	-55	19.0

Notice that the short 90% life and longer 80% life indicate a bad spike for the hot test. The cold test was quite linear and the room temperature test was somewhere between these. This is another indication that a thermal buffer may be necessary to prevent thermal shock from causing a spike at activation.

A couple other series of batteries have been constructed for storage tests. These will be tested at given intervals and reported later.

SECTION XIX

CONCLUSION

A commercial source of NaAlCl_4 has been found. As a result of this, electrolyte fabrication has become much faster, easier, more consistent and safer. Enough work has now been done with this material so that characteristic fingerprint DSC spectra are now available for all of the electrolyte materials used for this battery system. The DSC technique has also been used to monitor moisture contamination in the electrolyte powders. Moisture has also been found to be related to the catholyte particle size growth problem. While the exact nature of this problem is still unknown it is now possible to make high quality cells with these materials. It has been found that the problem doesn't exist with the CuCl_2 system.

The electrolyte binder experiments have demonstrated that the amount of Cab-O-Sil in an anolyte can be varied considerably without serious degradation of the electrical properties of the cell. Kaolin clay has been found to be an excellent binder that does not need to be fused into the salts and is therefore good for use with AlCl_3 rich electrolytes.

Other alternate materials studied have been alternate cathode materials. FeS_2 has been found to function well only at elevated temperatures and is not being further considered for work with this system. It has been concluded that MoCl_5 would make better high energy density batteries, while CuCl_2 is better suited for long life batteries. FeCl_3 had a good discharge profile immediately after activation although the life times are usually short. FeCl_3 might be considered for an impulse battery application. The behavior of WCl_6 is similar to CuCl_2 with the disadvantage of greater expense. During these alternate cathode studies it was observed that cells made from MoCl_5 catholytes produce higher energy densities

when discharged at higher current densities. CuCl_2 cells, on the other hand, produced higher energy densities when discharged slowly at low current densities. Cells made with FeCl_3 produce consistently regardless of the discharge rate.

Experiments have been done with alternate LiAl alloys with various results. Cells now have longer lifetimes and greater energy densities (see Figure 25). Also more insight has been gained about the nature of the activation high voltage spike. These facts are known about the spike.

- 1) Moisture contamination causes a spike.
- 2) Cells operating at low current density have a greater tendency to form a spike than cells operating at high current density.
- 3) The presense of LiCl in the anolyte can cause a spike.
- 4) Excessive Cab-O-Sil in the anolyte can cause a spike.
- 5) High temperatures aggravate the spike condition.
- 6) A smaller concentration of lithium in the anode reduces the spike.
- 7) The relative masses of anode to cathode in a cell or, of MoCl_5 to graphite in a catholyte effects the size and shape of the spike.
- 8) A catholyte which has been stored for a period of at least one month has a tendency to form a spike.
- 9) No spike has been observed with FeCl_3 and rarely with CuCl_2 .
- 10) No spike has been observed with cells made with LiSi anodes.

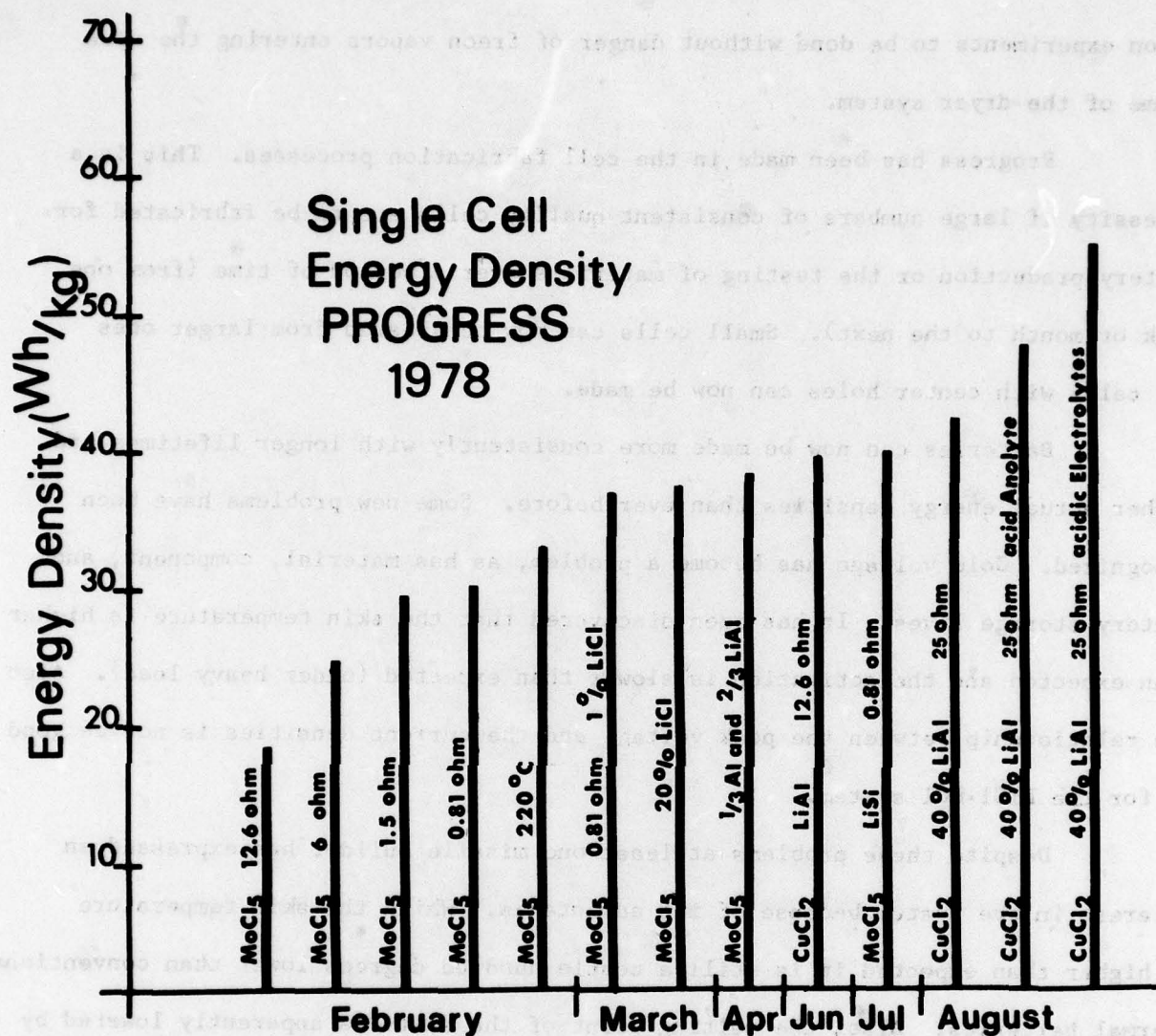


Figure 25. The Useful Energy Density of the Cell has nearly Tripled in One Year

A special fume hood has been constructed and is being installed in a dry room so that the freon blending process can be implimented. This will enable freon experiments to be done without danger of freon vapors entering the open flame of the dryer system.

Progress has been made in the cell fabrication processes. This is a necessity if large numbers of consistent quality cells are to be fabricated for battery production or the testing of materials over a period of time (from one week or month to the next). Small cells can now be sheared from larger ones and cells with center holes can now be made.

Batteries can now be made more consistently with longer lifetimes and higher actual energy densities than ever before. Some new problems have been recognized. Cold voltage has become a problem, as has material, component, and battery storage lives. It has been discovered that the skin temperature is higher than expected and the activation is slower than expected (under heavy load). Also the relationship between the peak voltage and the current densities is not as good as for the LiCl-KCl system.

Despite these problems at least one missile builder has expressed an interest in the system because of its advantages. While the skin temperature is higher than expected it is still a couple hundred degrees lower than conventional thermal batteries. Also, the melting point of the salts is apparently lowered by the cell reaction products, and this helps increase the battery life. The cell is capable of carrying a relatively large current.

In the next year the material and component studies will be continued. A reference electrode cell study will be started. Freon blending will be started and it is now time to pick one system and try to make a battery that will fill the stated goals of the contract.